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Attachment 3

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DATE: May 27, 2010

SUBJECT: HEXAZINONE RESIDUES IN CALIFORNIA GROUND WATER-MONITORING DATA PROVIDE EVIDENCE THAT DETECTIONS RESULT FROM LEGAL AGRICULTURAL USE

PURPOSE

To provide the Department of Pesticide Regulation's (DPR's) Environmental Monitoring Branch (EMB) management an analysis of well monitoring data and field studies linking hexazinone detections in ground water to legal agricultural use.

SUMMARY

Hexazinone, a persistent, mobile herbicide, was registered in California in the late 1970s. It is primarily used in the production of alfalfa and timber crops and, to a much lesser degree, on rights-of-way. Hexazinone's physical and chemical properties indicated that it was persistent and mobile and it was placed on Title 3, California Code of Regulations (3 CCR) section 6800(b) list in 1992. The DPR has currently analyzed over 3,800 samples from 2,300 wells for the presence of hexazinone residues and has detected these residues in California ground water intermittently since 1994 at levels ranging from 0.05 to 0.27 parts per billion (ppb) in 26 wells. These detections have largely occurred in alfalfa growing regions with a history of hexazinone use, but most have been isolated from other hexazinone detections. There have been three groups of detections.

The first group in Tulare County was determined to be the result of contamination by residues from a nearby landfill, a nonagricultural source.

Detections near Tracy, California were previously declared legal agricultural use (LAU) by EMB staff but a review by the Assistant Director of DPR stated that the detections were transitory and

directed more monitoring for evidence of movement of residues to ground water (Sanders, 1997, Gosselin, 1997). A follow-up study conducted in an alfalfa field near Tracy documented movement of residues in irrigation runoff water to a collection pond and ultimately in samples of shallow ground water that was recharged from the pond (Prichard, et al., 2005). Subsequent well monitoring in the area six years later determined that hexazinone residues continued to be present in one well but had dropped to below the reporting limit for the other. Monitoring in 2009 found hexazinone residues in two wells in two sections adjacent to the 2002 detection. Three wells in three adjacent sections provide evidence that hexazinone is migrating to ground water as a result of hexazinone use in alfalfa production.

Three recent detections of hexazinone within a one mile section in Fresno County provide further evidence that hexazinone is migrating to ground water as a result of hexazinone use in alfalfa production.

The pattern of the recent detections in San Joaquin and Fresno Counties fulfills the policy for the determination of LAU and hexazinone should be submitted for review as specified in the Food and Agricultural Code (FAC) section 13149 and added to the 3 CCR section 6800(a) list of regulated pesticides.

Hexazinone differs from the known ground water contaminants in that DPR does not consistently detect it in areas where it is used and in wells sampled repeatedly over time. This could be due to factors including:

- The main crop of use, alfalfa, is typically grown on fine soils which require additional runoff conditions to be present to allow pesticides to reach ground water.
- Compared to other commonly detected pesticides, hexazinone has low, infrequent and/or geographically dispersed use.
- Typical ambient ground water concentrations are at or near the reporting limit. This increases the chances of a well that has hexazinone residues being reported as “none-detected” based on sampling and analysis variability.

Regardless of factors that may affect the detection frequencies and concentrations, the data indicate that hexazinone has migrated to ground water as a result of its use in alfalfa production in California. If use expands as a result of pesticide label changes or increased alfalfa production, we would expect a commensurate rise in the detection frequency, and possibly the range of

concentrations, given its mobility and persistence. While additional monitoring may provide us with a better understanding of the relationship between application practices and potential contamination routes, DPR should initiate the regulatory actions to prevent further contamination.

BACKGROUND

Pesticide Use Profile

Hexazinone, an agricultural herbicide, was registered for use in California in the late 1970s. It can be applied before or after weed emergence, is readily absorbed by roots and foliage, and requires moisture for activation. The primary uses of hexazinone from 1995 to 2004 in California are in alfalfa production (~63%) and forestry (~34%) (CDPR, 2008) (Table 1). Applications to alfalfa typically occur yearly in December and January, when the crop is dormant and is recommended to be applied in the first two years of a four-year crop cycle. The recommended application rate is up to 1.5 pounds per acre. Product labels warn that agricultural use in permeable soils underlain by shallow water tables can cause hexazinone to contaminate ground water.

Table 1. Total pounds hexazinone used from 1995 to 2004 statewide and by county and crop. Only the counties with the verified hexazinone detections are shown. The overall rank for the county, based on total hexazinone usage statewide, is shown.

Total by Location			**Total by Site**				
			Alfalfa	Forests	Rights of way	Nursery plants	Bermuda grass (hay)
Statewide		1,117,280	707,876	378,214	11,279	8,094	3,226
County	**Rank**						
San Joaquin	1	114,194	114,085	0	0	0	0
Merced	3	92,275	88,495	0	4,269	0	0
Fresno	6	77,369	76,932	118	123	24	0
Solano	8	51,284	51,147	0	0	0	0
Stanislaus	11	41,971	41,956	0	15	0	0
Tulare	14	30,993	30,866	0	61	0	0
Colusa	18	11,421	11,384	0	32	0	0
Los Angeles	30	5,103	4,086	0	875	0	0

Environmental Fate

Hexazinone is very soluble in water (33,000 ppm at 25ºC), is not strongly adsorbed to soil organic material (average Koc = 41) and is moderately persistent with half-lives ranging from 100 to 136 days (Table 2). It is relatively stable in water but residues in the biologically active soil layers are susceptible to microbial degradation. Due to its solubility and Koc, hexazinone is more mobile than the other commonly detected herbicides registered for use in California and, with the moderate to long half-lives, can threaten both surface and ground water through run-off and leaching (Ganapathy, 1996).

Table 2. Comparison of hexazinone use and physical-chemical properties to other pesticides found in the ground water of California due to agricultural use.

Pesticide	Total Pounds AI applied[1]	Koc[2] ml/g OC (median)	Solubility ppm at 25ºC	Field half-life (range in days)
Hexazinone	1,117,280	41	33,000	100-136
Atrazine	558,065	114	33	92-141
Bromacil	730,138	20	700	146-1670
Diuron	13,285,692	386	36	103-133
Norflurazon	2,127,118	441	34	33-835
Prometon	302	100	394	307-1319
Simazine	7,470,810	84	6	36-153

DPR staff are developing an approach to prioritizing GWPL pesticides for monitoring. A component of the approach estimates potential residue concentrations in ground water using each pesticide's physical and chemical properties in a pesticide fate and transport model. This data is coupled to each pesticide's reported use data throughout California. The GWPL pesticides are then sequentially ranked based on these coupled data sets. Other non-quantitative features of each pesticide are considered in their ranking sequence. Examples of these are the presence of previous ground water detections and predominant site of application. Of the 101 active ingredients on the GWPL hexazinone is currently ranked second in terms of its relative risk to contaminate California ground water.

[1] Total pounds of active ingredient (AI) applied statewide from 1995 to 2004 for each pesticide derived from DPR's Pesticide Use Report database.
[2] The Koc, and field dissipation for each pesticide are derived from Troiano, 2009. Solubility taken from Spurlock, 2008.

Detection Verification

DPR began monitoring for hexazinone in 1993 following development of an analytical method for this pesticide (Weaver and Marade, 1993). In 1994, DPR included hexazinone in a multi-analyte screen used to monitor for known ground water contaminants. These early analytical methods did not allow DPR to unequivocally identify detected contaminants. As required by the Pest Contamination Prevention Act, DPR verified hexazinone detections by analyzing additional samples using a second analytical method or a second analytical laboratory. The reporting limit (RL) for the primary sample was typically higher than that used by the verifying laboratory. RLs for the different laboratories and methods ranged between 0.05 to 0.2 ppb. Samples that had hexazinone levels below the primary RL would only have been sent in for verification if there were other pesticide residues detected in the primary sample. In 2001, the California Food and Agriculture Department (CDFA) Center for Analytical Chemistry began using liquid chromatography/mass spectrometry analysis, which allowed unequivocal identification of the regulated ground water contaminants and their main degradates, norflurazon and its main degradate, and hexazinone (CDFA, 2001; Fattah, 2008). The unequivocal method allowed for a uniform RL for all chemicals. In 2002, three hexazinone degradates[3] were temporarily added to this screen to allow DPR to conduct a focused survey in the areas of highest hexazinone use. These degradates were later dropped from the screen due to very low detection rates.

The RL for the current multi-analyte screen is 0.05 ppb and is set 1 to 5 times greater than the method detection limit[4] to account for analytical variability. Results at or above the RL are reported as numeric values. Although it is possible to quantify results that fall between the RL and the method detection limit, the Ground Water Protection Program reports all results that are less than the RL as "none-detected" to decrease the chance of reporting false positives.

Detections Reported by Other Agencies

Hexazinone has also been detected in California's ground water by other agencies. From 2001 through 2007, the U.S. Geographical Survey (USGS) National Water-Quality Assessment Program detected hexazinone in 70 wells in 16 states with concentrations ranging from 0.003 ppb to 1.13 ppb (USGS, 2008a). California had the second highest detection frequency with 12 positive wells in eight counties, including Central Valley counties where DPR also detected hexazinone, at levels from 0.005 to 0.04 ppb. The USGS, under contract with the State Water Resources Control Board's Ground water Ambient Monitoring Assessment program, also detected hexazinone in 28 wells with concentrations as high as 0.066 ppb (USGS, 2008b, personal communication M. Fram). DPR has received some preliminary data for 23 wells with hexazinone residues. Two of the USGS detections are above our 0.05 ppb RL at 0.066 and

[3] 2-hydroxycyclohexyl hexazinone, monomethyl hexazinone, and decyclohexyl-4-hydroxy hexazinone.
[4]The lowest concentration of analytes that a method can detect reliably in a sample.

0.062 ppb and a third had a concentration of 0.041 ppb. Follow-up field studies will be initiated for these three detections when further details can be obtained from USGS. DPR requested these data in 2008. The remaining wells have concentrations below 0.02 ppb.

Drinking Water Quality Standards

There are no state or federal regulatory standards or public health goals for hexazinone in drinking water. The U.S. Environmental Protection Agency established several non-regulatory drinking water health advisories including a Lifetime Health Advisory[5] of 400 µg/L, a Drinking Water Equivalent Level[6] of 2000 µg/L, and a Reference Dose[7] of 50 µg/kg/day. The hexazinone concentrations found by DPR in California's ground water fall far below these levels. Because there are no regulatory standards established for hexazinone, it is not included in the standard pesticide screens required by the California Department of Public Health for public water wells.

RESULTS

DPR included hexazinone in the Ground Water Protection List (GWPL) (3 CCR section 6800[b]) due to its persistence and mobility and intentional applications to soil. In 1993, DPR began sampling for hexazinone soon after identifying it as a monitoring priority based on reported detections in ground water in other states (Weaver and Marade, 1993). Since then, DPR analyzed 3,824 samples from 2,345 wells for the presence of hexazinone (CDPR, 2009). Hexazinone was detected in 34 samples from 26 wells with concentrations that ranged from 0.05 to 0.27 ppb (Table 3). All hexazinone detections reported in this document were either verified by a second analytical laboratory or analyzed using an unequivocal method.

Whenever DPR detects a pesticide in a well, additional monitoring is conducted near the original detection to determine the spatial extent and the potential source of the contamination (CDPR, 1996). The detection pattern for hexazinone is somewhat different than that of a typical ground water contaminant in that 15 of the 26 positive wells are isolated from other hexazinone detections (> 1 mile apart). Other wells have been sampled in the areas surrounding these wells and none were found with hexazinone residues. Isolated detections have occurred in Colusa, Fresno (locations 14S21E21 and 14S22E13), Los Angeles, Merced, San Joaquin (location 01N05E16 and 02S04E22), Solano, and Stanislaus Counties. The remaining eleven positive wells are located in three groups in Fresno (3 wells, location 17S19E36), San Joaquin (4 wells,

[5] Lifetime Health Advisory is the concentration of a chemical in drinking water that is not expected to cause any adverse noncarcinogenic effects for a lifetime of exposure (70-kg adult consuming 2 liters of water per day).
[6] Drinking Water Equivalent Level is a lifetime exposure concentration protective of adverse, noncancer health effects, that assumes all of the exposure to a contaminant is from drinking water.
[7] Reference Dose is an estimate of a daily oral exposure to the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious effects during a lifetime.

locations 02S05E23, 02S05E24, 02S06E19, and 02S06E30) and Tulare (4 wells, locations 22S27E07 and 22S27E18) Counties.

The Tulare County group was determined to result from a point source contamination (Goh, 1995). This data will not be submitted to the review process because the contamination was not the result of LAU.

The San Joaquin County group near Tracy was determined to result from LAU but was suspected of being transitory requiring further monitoring (Gosselin, 1997). Subsequent monitoring in San Joaquin County found one of the two wells still had hexazinone residues present six years later indicating the residues in that well were not transitory. Additional wells were sampled but no further wells were found with hexazinone residues. At that point, with only one well with hexazinone residues remaining, there was not enough data to reenter the review process as specified in the FAC section 13149. In 2009, two more wells with hexazinone residues were found in sections adjacent to the one with the “non-transient” well. All of these sections have a history of hexazinone use. This data is being into the review process.

In the third case, hexazinone was detected in three wells in a single section in Fresno County near Riverdale. This section has a history of hexazinone use and alfalfa production and no point sources were found during the field surveys. The source has been evaluated by DPR and determined to be due to LAU (Nordmark, 2008). This data is being into the review process.

The total reported use of hexazinone in the area surrounding the 26 positive wells varies from zero to thousands of pounds for the 6 to 16 year period prior to detection. The Tulare group of four wells and three isolated wells located in Colusa, Fresno (location 14S22E13) and Los Angeles had no apparent history of hexazinone use. However, all but three of the positive wells, including the Tulare detections, were located in or adjacent to sections where alfalfa has been grown from 1990 to 2005 based on pesticide use reports. The three wells with no alfalfa grown in their proximity were located in Fresno (locations 14S21E21 and 14S22E13) and Los Angeles Counties. Therefore only two of the 26 positive wells (Fresno County location 14S22E13 and the Los Angeles County detection) were in areas where there is no record of either hexazinone use or alfalfa cultivation. Only the Tulare group has an obvious point source for hexazinone contamination. The potential agricultural sources combined with a lack of obvious point sources for the remaining 20 positive wells suggest agricultural use is the likely cause of these detections. However, only the seven wells in the Tracy and Riverdale groups meet the standards of proof for LAU required by DPR.

Table 3. Hexazinone sampling results and pesticide use information for areas where hexazinone residues have been detected. Specific well information is located in Appendix 1.

County	Location[8]	Wells Sampled For Hexazinone	Hexazinone Positive Wells[9]				Hexazinone Use (LBS)[10]	
			Unique Positive Wells	Highest conc. (ppb)	First Year Detected	Last Year Sampled	Single Section	Nine-Sections[11]
Colusa	15N03W36	2	1	0.056	1998	1998	0	0
Fresno	14S21E21	3	1	0.063	2001	2006	0	14
Fresno	14S22E13	3	1	0.07	2000	2006	0	0
Fresno	17S19E36	4	3	0.274	2007	2008	320	2,155
Los Angeles	01S09W27	1	1	0.069	2008	2008	0	0
Merced	09S14E23	3	1	0.11	1997	1997	347	826
San Joaquin	01N05E16	2	1	0.092	2008	2008	541	4,937
San Joaquin	02S04E22	5	1	0.096	2002	2002	625	2,288
San Joaquin	02S05E23	2	1[12]	0.11	1996	2002	216	1,130
San Joaquin	02S05E24	6	1[12]	0.07	1996	2002	435	2,642
San Joaquin	02S06E19	3	1	0.072	2009	2009	171	3,214
San Joaquin	02S06E30	1	1	0.093	2009	2009	178	3,615
Solano	06N01E05	4	1	0.094	2002	2002	0	2,650
Solano	06N01E23	2	1	0.126	2007	2007	1198	7,644
Solano	06N01W36	4	1	0.092	1995	1995	788	1,763
Stanislaus	04S09E19	5	1	0.27	1996	1996	7	484
Stanislaus	04S11E31	5	1	0.263	2004	2004	152	1,422
Stanislaus	06S08E26	2	1	0.062	2007	2007	80	720
Stanislaus	07S08E14	1	1	0.073	2001	2002	0	125
Stanislaus	07S09E06	2	1	0.094	2007	2007	102	1,088
Tulare	22S27E07	1	1[13]	0.22	1994	1995	0	0
Tulare	22S27E18	6	3[13]	0.24	1994	1995	0	0

[8] Township, range and section of the well(s). A section is approximately one square mile.
[9] Data in these columns apply only to wells that have had at least one sample with a hexazinone concentration above the reporting limit.
[10] Hexazinone use totals are given for one of three periods, 1990-95, 1990-2000 and 1990-2005, based on the year of the first detection in the section. The period used was selected to represent the hexazinone use prior to the first reported hexazinone detection. Since full pesticide user reporting began in 1990, the 1990-95 bracket was used for detections prior to 1996. Rights-of-way use is reported at the county level and is not included here.
[11] Total hexazinone use in the section where the positive well is located and the surrounding 8 sections.
[12] Detections were determined to be transitory (Gosselin, 1997) and later due to agricultural drainage ponds (Prichard, et al., 2005). Wells were resampled in 2002. The positive well in section 24 still had residues, the positive well in section 23 did not.
[13] Detections resulted from point source contamination.

DISCUSSION

When pesticide residues are found in the ground water of the state, DPR is required by the FAC section 13149 to make a determination as to whether those residues resulted from LAU in accordance with state and federal laws and regulations, and must state in writing the reasons for the determination. The two applicable criteria for making the LAU determination include:

1. The pesticide ingredient is verified in a second well in the same or adjacent one-square mile section of land. This was originally stated as a second well within one-half mile (Oshima, 1987) but was subsequently revised to two wells within a four-section area (Goh, 1992).
2. The pesticide has been reported used in the vicinity or there are sites within the section where the pesticide ingredient might have been used (Oshima, 1987).

DPR has detected hexazinone residues in 26 wells in eight counties (Table 3, Appendix 1, and Appendix 2). Eleven of these wells are located in three groups of wells in adjacent sections and the remaining 15 are isolated from other hexazinone detections. LAU determinations have been conducted for all three groups, Tulare, San Joaquin County near Tracy and Fresno County near Riverdale. The source of residues in the San Joaquin County near Tracy well group has been reinvestigated based on two new hexazinone detections. The determinations for the hexazinone detections are as follows:

1. Four wells in Tulare County (Figure A14) with hexazinone residues in two adjacent sections were determined to be due to the Teapot Dome Landfill, a point source. (Goh, 1995). Two of the wells were domestic wells and two were monitoring wells installed at the edge of the landfill. No hexazinone was reported used in the area but there was some alfalfa grown in the section where three of the wells were located and in several of the adjacent sections.

2. Two wells in San Joaquin County in two adjacent sections (02S/05E-23 and 24) east of Tracy had hexazinone residues (Figure 1.). Hexazinone was used on alfalfa in these sections. As reported in the study memorandum (Weaver 1997), detections of atrazine, diuron, and hexazinone near Tracy, California were related to agricultural use patterns An investigation by the Pesticide Enforcement Branch revealed the presence of agricultural runoff pits in the vicinity of the contaminated wells. There was no evidence that the pits had been used to dispose of pesticides or pesticide containers-potential point sources. However, the investigation identified the pits as a potential nonpoint source pathway because they collected potentially contaminated irrigation runoff from nearby fields (Sanders, 1997).

   The detections for atrazine and diuron were included in an analysis of major soil properties that were representative of sections of land with known contamination (Troiano et al., 2000). These areas were identified as a soil cluster that was fine textured and that exhibited a winter

seasonal water table within 1.5 meter of the soil surface. These properties reflect those of cracking-clay soils. In addition to recharge from the pits adjacent to agricultural fields, it was also thought that the cracks on the clay soils could enhance the rapid downward movement of residues within the agricultural fields. The EMB determined that these residues were the result of LAU. However the Assistant Director for DPR stated that the detections were transient and did not meet the criteria for a LAU determination (Gosselin, 1997). DPR conducted further monitoring in this area and obtained the following results:

a. The two hexazinone wells were resampled in 2002 by DPR. One well still had hexazinone residues present and one did not.

b. Two additional wells with hexazinone residues were found in two sections (02S/06E-19 and 30) adjacent to the non-transient well section (02S/05E-24) in 2009 as part of a ground water monitoring study. These new detections have been investigated and determined to be due to LAU (Nordmark, 2010). All three sections have a history of hexazinone use on alfalfa and all sections have runoff ponds present. No evidence of point source contamination was found.

c. A cooperative study was initiated with the University of California, Davis farm advisors to document movement of hexazinone and diuron residues in an alfalfa field (Prichard et al., 2005). An alfalfa field was identified where the major soil type was a cracking-clay soil and runoff water was collected in an adjacent pond. The herbicides were applied in December 1999. The fate of the herbicide residues was determined from soil samples taken within the field, water runoff samples sampled after two border check irrigations, the water in the adjacent pond, and shallow ground water sampled near the pond. After six months, residues were confined to the first 15 cm of soil, indicating very little effect of the macro-pores in facilitating downward movement within the field. In this case, the clayey soil cracks upon prolonged drying but rapidly hydrates during the winter rainy season which causes the cracks to rapidly disappear. The results were as follows:

   i. Residues of hexazinone and diuron were measured in runoff and pond water that was generated from border-check irrigations. Measurements taken from devices to monitor the volume of pond water and the depth of the water table near the pond indicated rapid downward movement of pond water and recharge of the ground water. Depth to ground water in this locale was around 4.5 m but excavation of the pond resulted in even shallower depths below the pond. Hexazinone residues were measured in the runoff water, the pond water, and in the shallow ground water sampled near the pond.

   ii. This study confirmed the observations (Sanders, 1997) that water collected into ponds adjacent to agricultural fields was a source of recharge of water that contained residues applied to the agricultural fields.

3. Two wells were located in section 17S/19E-36 in Fresno County near Riverdale (Figure 2 and Figure A13) as part of a 2008 monitoring study. A follow up study (Z573) to these two detections found an additional well with hexazinone residues in the same section. These three detections have been determined to be due to LAU (Nordmark, 2008). There is a record of hexazinone applications in the area and fields currently planted in alfalfa were observed. An unlined canal runs through the section near two of the wells and several small runoff ponds are present. The measured depth-to-water for the Z573 hexazinone well was 119 feet which was consistent with other measured water depths in the area.

4. DPR was unable to make a LAU determination for the remaining 15 hexazinone detections because no other wells with hexazinone residues could be found within one mile of the detection with hexazinone residues. Three of these wells in Stanislaus County near Newman (Figure A9) are spaced approximately 2.8 miles apart, putting them one section away from qualifying for a LAU determination. The depth-to-ground water in this area is less than 50 feet, there is low hexazinone use but there is a record of alfalfa being grown. Five of the 15 ungrouped wells are located in current GWPAs (Marade and Troiano, 2000a). Nine of the ten remaining hexazinone residue wells, including the three near Newman, are in areas that lack sufficient soil data for the model to determine GWPA status. Thirteen of the wells are located in or adjacent to sections where alfalfa has been grown from 1990 to 2005 based on pesticide use reports.

There may be several reasons why the detections of hexazinone are so sporadic even though our modeling indicates the pesticide should be prone to reaching ground water.

1. The primary use of hexazinone is on alfalfa, which is typically grown on fine textured soils. These soils are generally impermeable and are more likely to result in offsite movement of pesticide residues via runoff than by leaching. Runoff can move to ground water via sensitive sites such as dry wells, drainage ponds and unlined ditches. However, not all alfalfa growing regions may have these sensitive sites nearby.

2. Total hexazinone use and application rates are relatively low compared to other herbicides more commonly found in the ground water of California (Table 2). Typical application rates are one pound per acre per year applied in the dormant season. The application rate for alfalfa grown on coarse soils is lower. In addition, hexazinone may only be applied in the first two years of a four-year alfalfa production cycle, whereas simazine, diuron, bromacil, and norflurazon are more likely to be applied annually to permanent crops. The total pounds applied for the more commonly found herbicides, simazine and diuron, are almost 6 to 12 times the total pounds of hexazinone used. Further, hexazinone has only very limited use on rights-of-ways compared to simazine, diuron, bromacil, and norflurazon.

3. Most hexazinone residue levels detected are near the RL and the RL is not zero. If the level is lower than the RL, it is reported as 'None-detected', not trace. Up until 1997, the RL for hexazinone in the primary sample for most DPR studies was 0.2 ppb. The back-up sample, which would only be analyzed if any pesticide was detected in the primary sample, was sent to a different lab or analyzed by a different method to confirm the detection. The second method usually had a lower RL than the primary method of either 0.05 or 0.1 ppb. The median residue level reported for detections, excluding those that could not be confirmed (one well each in Imperial and San Joaquin Counties) or were determined to be point sources (Tulare County), is 0.07 ppb. Additionally, residue levels vary over time as shown by DPR's long term monitoring studies. If a hexazinone level is hovering around the RL, the date of the sampling might determine whether or not hexazinone is detected in a specific well. Over 75% of the detections under discussion are below the original 0.2 ppb detection limit used for the primary samples prior to 1997 and 60% are below the 0.1 ppb limit used for the primary samples prior to 1997. Four of the 25 wells with hexazinone residues had no other pesticide residues detected. Such wells might have been missed if sampled prior to 1997. If the original RL had been 0.05 ppb for the primary sample, we would expect to have additional wells with hexazinone residues possibly providing additional evidence for LAU.

Other studies have shown that hexazinone levels in treated areas are relatively low. In a Canadian ground water study of an area of course soils that had been planted in blueberries and treated with hexazinone for over 20 years (Keizer et al. 2001), groundwater was sampled for hexazinone at different depths. The blueberries are treated with hexazinone biennially at a rate of 1.28 pounds per acre. This study found that hexazinone was broken down by microorganisms in the aerobic zone of the soils and shallow ground water. Parent residue levels in the shallow ground water ranged from 1 to 8 ppb. Further degradation occurs in the anoxic zone where the parent level ranged from below the detection limit (<0.02 ppb) to 0.3 ppb. Nineteen of 21 wells in the study area had residues of hexazinone. The only wells in the study without detections were either upgradient of the applications or had anoxic conditions. These results indicate that hexazinone is degraded in both aerobic and anoxic ground water zones.

Hexazinone use on alfalfa in California is typically on fine soils where the path of contamination appears to involve runoff of pesticide residues to sensitive areas. Sensitive sites must be present for residues to reach ground water, but when these sites are present, they would provide a more rapid conduit to the anoxic ground water zones. This could be one factor in the typically low levels detected in our studies. Even in the coarse soils of the Keizer et al. study, the maximum residues in anoxic ground water was 0.3 ppb.

There is not always a clear link between hexazinone use and the presence of residues in the ground water. Of the 20 sections with detections, 12 have a record of hexazinone use in the sampled section and 15 sections have reported use in the nine-section area (Table 3). All of the sections where a second confirming well has been found have reported use of hexazinone. An

additional factor in determining LAU is the presence of sites where the pesticide could have been applied. The pesticide use report indicates that alfalfa was being grown in or adjacent to 17 of the sections where hexazinone has been found. The three exceptions are the two isolated sections in Fresno County (14S/21E-21 and 14S/22E-13) and the detection in Los Angeles County (01S/09W-27). Although there appears to be a lack of applications or legal use sites near several detections, this may be of less importance when other factors are considered, including the potential for hexazinone residues to travel long distances in irrigation run-off water or gaps in the Pesticide Use Reporting data related to applications that are reported by county not by site such as rights-of-way applications. Another potential explanation relates to the lack of hexazinone use information prior to 1990 when California began full pesticide use reporting. It is possible that there were potential application sites and/or hexazinone applications in these areas prior to 1990.

CONCLUSIONS

Current and historical monitoring data strongly suggest that the agricultural use of hexazinone, primarily in alfalfa production, has resulted in its migration to ground water in California.

Three 2008 detections in Fresno County, section 17S/19E-36, meet DPR's current agricultural use determination policy of two or more detections within the same or adjacent one-square mile sections of land, reported use of hexazinone in the section and the surrounding area, and no evidence of point source contamination. Two 2009 detections of hexazinone in San Joaquin County, sections 02S/06E-19 and 30, also meet this agricultural use determination policy criteria. In addition, these 2009 detections are adjacent to a section, 02S/05E-24, where hexazinone was detected in a well in 1996 and again in 2002. However, in evaluating the need for further regulatory actions, the isolated detections in Merced, San Joaquin, Solano and Stanislaus Counties, should also be considered due to the proximity of these detections to reported hexazinone applications and/or areas where alfalfa has been grown. These detections all contribute towards a preponderance of the evidence that hexazinone is reaching ground water due to legal agricultural use.

Further monitoring in the vicinity of the isolated detections may not yield additional data. In most cases, all of the wells that are suitable for sampling and for which permission could be obtained from the well owner, have been sampled. However, DPR will continue to sample ground water for hexazinone as part of our on-going monitoring programs and will respond to additional hexazinone detections.

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Approved: __*Original signed by*_____ Date:_____
Lisa Ross, Ph.D. Environmental Program Manager

bcc: Nordmark Surname File

Figure 1. Wells sampled by DPR in the GW09/Z574 study area showing wells with hexazinone residues, wells with pesticide residues other than hexazinone, and wells with no residues detected. A view of the same area with detected residues is shown in figure A5 in Appendix 2. All wells shown were tested for hexazinone. GW09/Z574 well location numbers are shown.

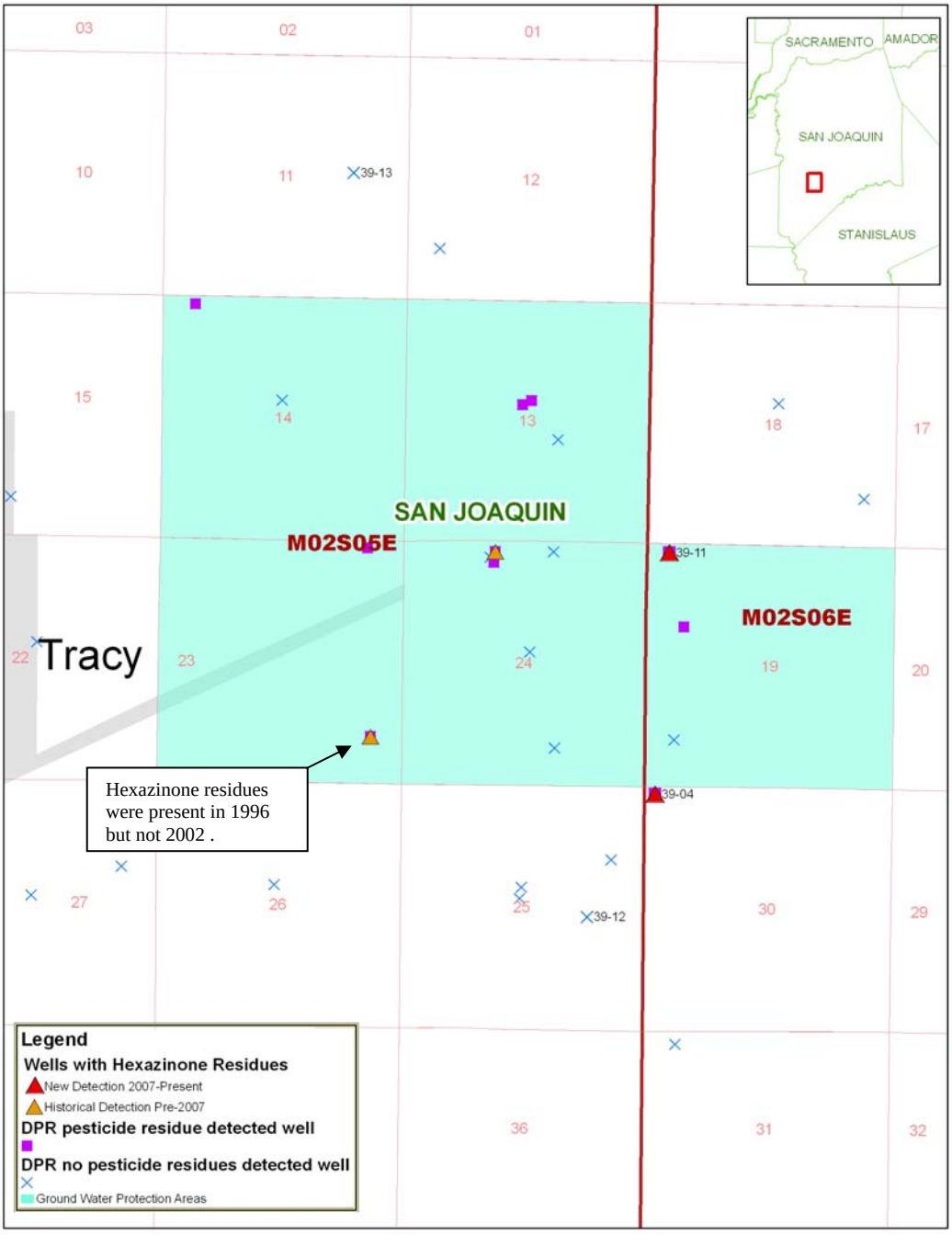
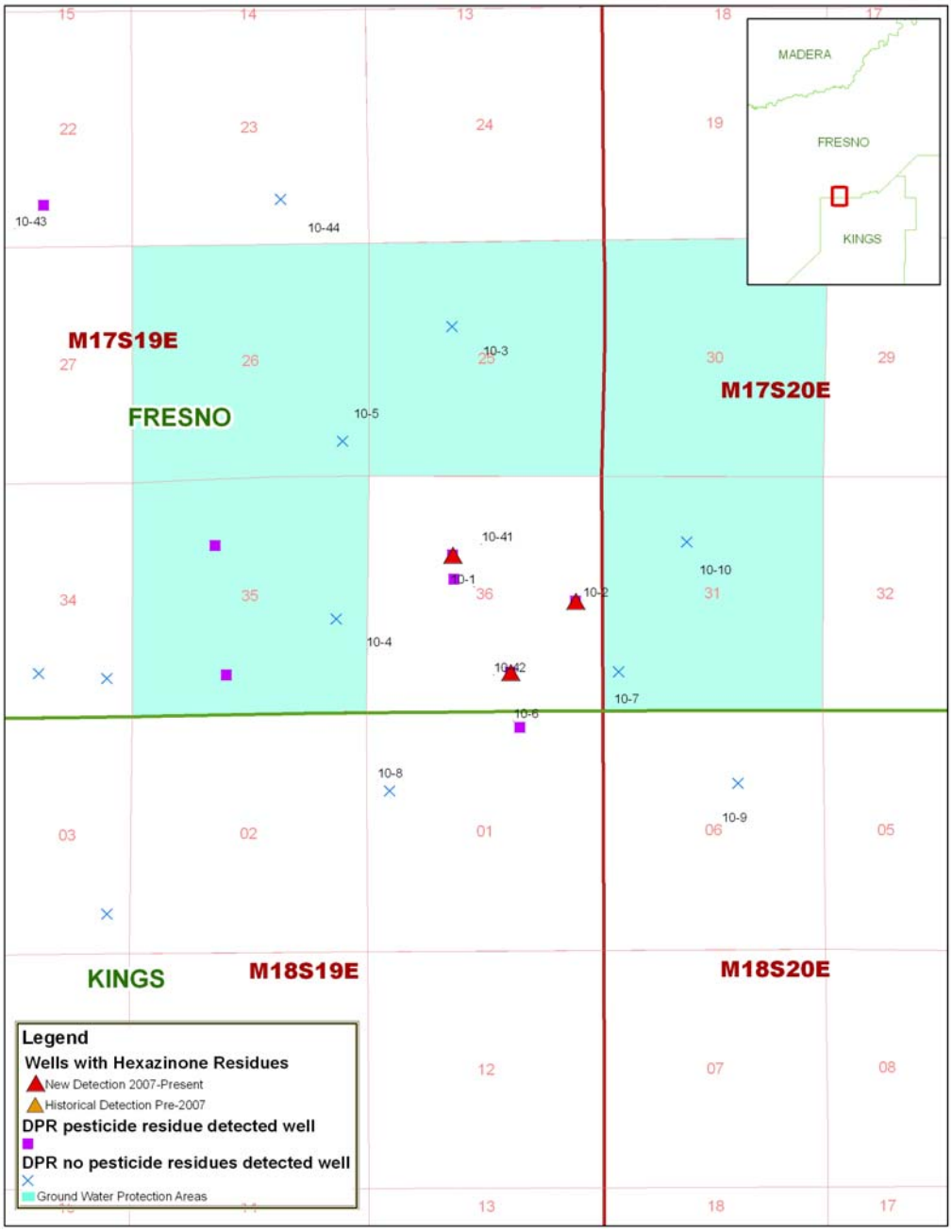


Figure 2. Wells sampled by DPR in the Z573 study area showing wells with hexazinone residues, wells with pesticide residues other than hexazinone, and wells with no residues detected. A view of the same area with detected residues is shown in figure A12 in Appendix 2. All wells shown were tested for hexazinone. Location numbers for study 240 and Z573 are shown.



Appendix 1. Hexazinone residue detections by DPR in California wells. Sections are linked to the associated map in Appendix 2. All analyzed samples, including backups, are shown for wells with confirmed detections.

COUNTY	SECTION	WELL ID	SAMPLE DATE	RESULT (PPB)	INITIATING STUDY AND NOTES
Colusa	15N03W36	1	09-MAR-94	ND	Z260[14]
			30-JUN-98	0.056	Initial Detection GW98. Field study Z414 found no residues in surrounding wells.
			15-MAY-07	ND	GW07[15]
Fresno	14S21E21	1	04-AUG-99	ND	WN[16]
			14-MAR-00	ND	WN
			08-NOV-00	ND	WN
			21-MAR-01	0.05	WN
			24-OCT-01	0.063	Initial detection WN. Z022 and study 226 found no residues in surrounding wells.
			01-APR-02	ND	WN
			28-OCT-02	0.062	WN
			06-MAY-03	ND	WN
			25-MAY-04	ND	WN
			27-JUN-05	ND	WN
			14-JUN-06	ND	WN
			09-MAY-07	ND	WN
			13-MAY-08	ND	WN
	14S22E13	1	28-MAR-94	ND	WN
			16-AUG-99	ND	WN
			15-MAR-00	0.07	Initial detection WN. Several field studies found no residues in nearby wells. Continued monitoring as part of Well Network.
			07-NOV-00	ND	WN
			19-MAR-01	ND	WN
			31-OCT-01	ND	WN
			30-APR-02	ND	WN
			28-OCT-02	ND	WN
			29-APR-03	ND	WN
			08-JUN-04	ND	WN
			20-JUN-05	ND	WN
			13-JUN-06	ND	WN

[14] "Z" studies are conducted in response to a reported detection of pesticides in ground water. These four-section surveys seek to sample additional wells in the area around the detection. Additional sections may be included in the study area. The original well may be resampled.
[15] "GW" studies are ground water studies targeting areas where specific pesticides are used. In most years each well sampled is also tested for a standard suite of pesticides.
[16] "WN" = Well network study. The wells in this study are sampled yearly to measure changes in pesticide levels.

COUNTY	SECTION	WELL ID	SAMPLE DATE	RESULT (PPB)	INITIATING STUDY AND NOTES
Fresno cont.	17S19E36	1	26-SEP-07	0.081	Study 240. Field study (Z573) found one additional well (well 3) with hexazinone residues found in section.
		2	26-SEP-07	0.247	Study 240. Field study (Z573) found one additional well (well 3) with hexazinone residues found in section.
		3	23-JAN-08	0.127	Z573 follow-up detection to 2 hexazinone wells in this section from study 240.
Los Angeles	01S09W27	1	16-APR-08	0.069	GW08. Currently under investigation. No residues found in two nearby wells.
Merced	09S14E23	1	05-NOV-97	0.11	GW97. Field study Z410 found no residues in nearby wells.
San Joaquin	01N05E16	1	10-JUN-08	0.092	GW08. Currently under investigation. One other well in section did not have hexazinone residues.
	02S04E22	1	08-OCT-02	0.096	GW03. Field study Z545 found no hexazinone residues in five nearby wells.
	02S05E23	1	08-AUG-96	0.092	Z385.
			03-OCT-96	0.11	Z385 resample. Field study found additional residues in nearby wells. Residues determined to be transitory.
			07-OCT-02	ND	GW03.
	02S05E24	1	08-AUG-96	0.07	Z385.
			03-OCT-96	0.063	Z385 resample. Field study found additional residues in nearby wells in 02S05E23. Residues determined to be transitory.
			07-OCT-02	0.05	GW03. Well resampled for a subsequent study.
	02S06E19	1	20-JUL-09	0.072	GW09.Currently under investigation. No residues found in two nearby wells in 1996.
	02S06E30	1	28-APR-09	0.093	GW09 Currently under investigation.
Solano	06N01E05	1	03-APR-02	0.094	Z455. GW03 and Z520 Field studies found no additional residues in nearby wells.
	06N01W36	1	21-MAR-95	ND	Z289. Primary sample. RL 0.2 ppb.
			21-MAR-95	0.092	Z289. Backup sample. RL 0.05 ppb.
			21-MAR-95	0.064	Z289. Backup sample. RL 0.05 ppb. Z289, study 240 and GW08 failed to find additional hexazinone residues in five nearby wells.
	06N01E23	1	06-FEB-07	0.126	Study 240. Currently under investigation. Four wells previously tested in the potential four-section survey area had no hexazinone residues.
Stanislaus	04S09E19	1	06-AUG-96	0.27	GW96. Z404 field study found no residues in six nearby wells.

COUNTY	SECTION	WELL ID	SAMPLE DATE	RESULT (PPB)	INITIATING STUDY AND NOTES
Stanislaus cont.	04S11E31	1	03-AUG-94	ND	Z262. No residues detected in initial sampling.
			09-AUG-04	0.263	Z558. Z558 and GW02 field studies found no residues in five nearby wells.
	07S08E14	1	15-AUG-01	0.06	GW01
			08-APR-02	0.073	Z448. Z448 and GW01 field studies found no residues in five nearby wells.
	06S08E26	1	14-MAR-07	0.062	Study 240. Currently under investigation. Limited availability of additional wells. Four wells previously tested in the potential four-section survey area had no hexazinone residues.
	07S09E06	1	14-AUG-01	ND	GW01.
			13-MAR-07	0.094	Study 240. Currently under investigation. Limited availability of additional wells. Three wells tested in the four-section area had no hexazinone residues.
Tulare	22S27E07	1	24-AUG-94	ND	AS94[17]. Primary sample. RL=0.2 ppb.
			24-AUG-94	0.16	AS94. Backup sample. RL=0.05 ppb. Residues determined to be from a point source.
			01-MAR-95	0.21	Z279. Primary sample. RL=0.2 ppb.
			01-MAR-95	0.22	Z279. Backup sample. RL=0.05 ppb.
	22S27E18	1	01-MAY-95	0.24	Z279. Monitoring well. Residues determined to be from a point source.
		2	01-MAY-95	0.21	Z279. Monitoring well. Residues determined to be from a point source. RL=0.05 ppb.
			01-MAY-95	0.19	Z279. Backup sample. RL=0.05 ppb.
		3	24-AUG-94	ND	AS94. Primary sample. RL= 0.2 ppb.
			24-AUG-94	0.084	AS94. Backup Sample. RL=0.05 ppb. Residues determined to be from a point source.
			24-AUG-94	0.095	AS94. Backup Sample. RL=0.05 ppb. Residues determined to be from a point source.
			01-MAR-95	ND	Z279. Primary sample. RL= 0.2 ppb.
			01-MAR-95	0.16	Z279. Backup sample. RL=0.05 ppb.

[17] "AS"=Adjacent Section studies were conducted around areas where pesticides had been previously been detected and designated as a Pesticide Management Zone.

Appendix 2 – Maps showing historical and current hexazinone detections in California.

Figure A1-a to A1-d are overview maps of all of the hexazinone detections by DPR in the state of California, both historical and current shown in relation to current Ground Water Protection Areas, hexazinone use, alfalfa growing areas, and all wells that DPR has tested for hexazinone.

Figures A2-A16 are detail maps of the areas around the historical and current wells with hexazinone detections. Each map shows one or more wells hexazinone residues were reported and:

- the location of wells sampled by DPR prior to study 240 where hexazinone was one of the pesticides in the analysis and the sampling results (positive or negative).
- the location of wells sampled by DPR as part of study 240, Z573, Z574, GW08 and selected GW09 and the results (current positive, or negative).
    - Wells with current pesticide detections also include the residue levels, in ppb, for each pesticide parent compound or degradate detected during the most recent sampling events.

The following pesticide abbreviations are used in Figures A2 through A15 to indicate the pesticide active ingredients or degradates detected by DPR. Parent compounds are in uppercase and degradates are listed in lowercase text.

Abbreviation	Pesticide active ingredient or degradate
acet	deethyl-simazine
ALesa	alachlor ESA
ALoxa	alachlor OXA
ATR	Atrazine
BRO	Bromacil
dact	diaminochlorotriazine
DBCP	1,2-Dibromo-3-chloropropane
dea	deethyl-atrazine
DIU	Diuron
dsmn	desmethyl-norflurazon
HEX	Hexazinone
hhex	2-hydroxycyclohexyl hexazinone
Mesa	metolachlor ESA
Moxa	metolachlor OXA
NOR	Norflurazon
PRO	Prometon
SIM	Simazine
TEB	Tebuthiuron
teb104	Tebuthiuron degradate 104

Figure A1-a. Statewide detections of hexazinone in well water and Ground Water Protection Areas. At this scale, a single triangle may cover multiple wells in the same area.

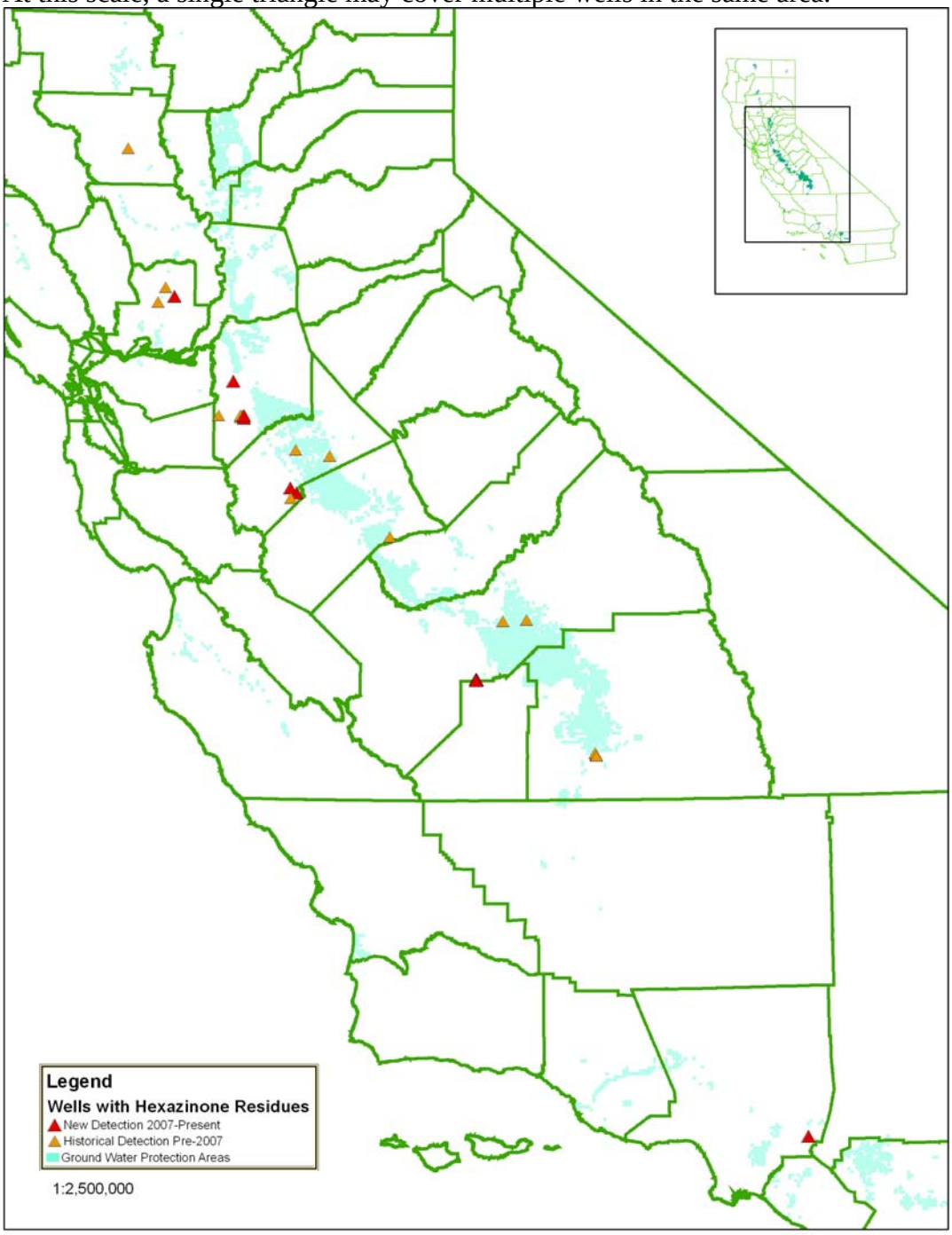


Figure A1-b. Statewide detections of hexazinone in well water and hexazinone applications 1990-2005. At this scale, a single triangle may cover multiple wells in the same area.

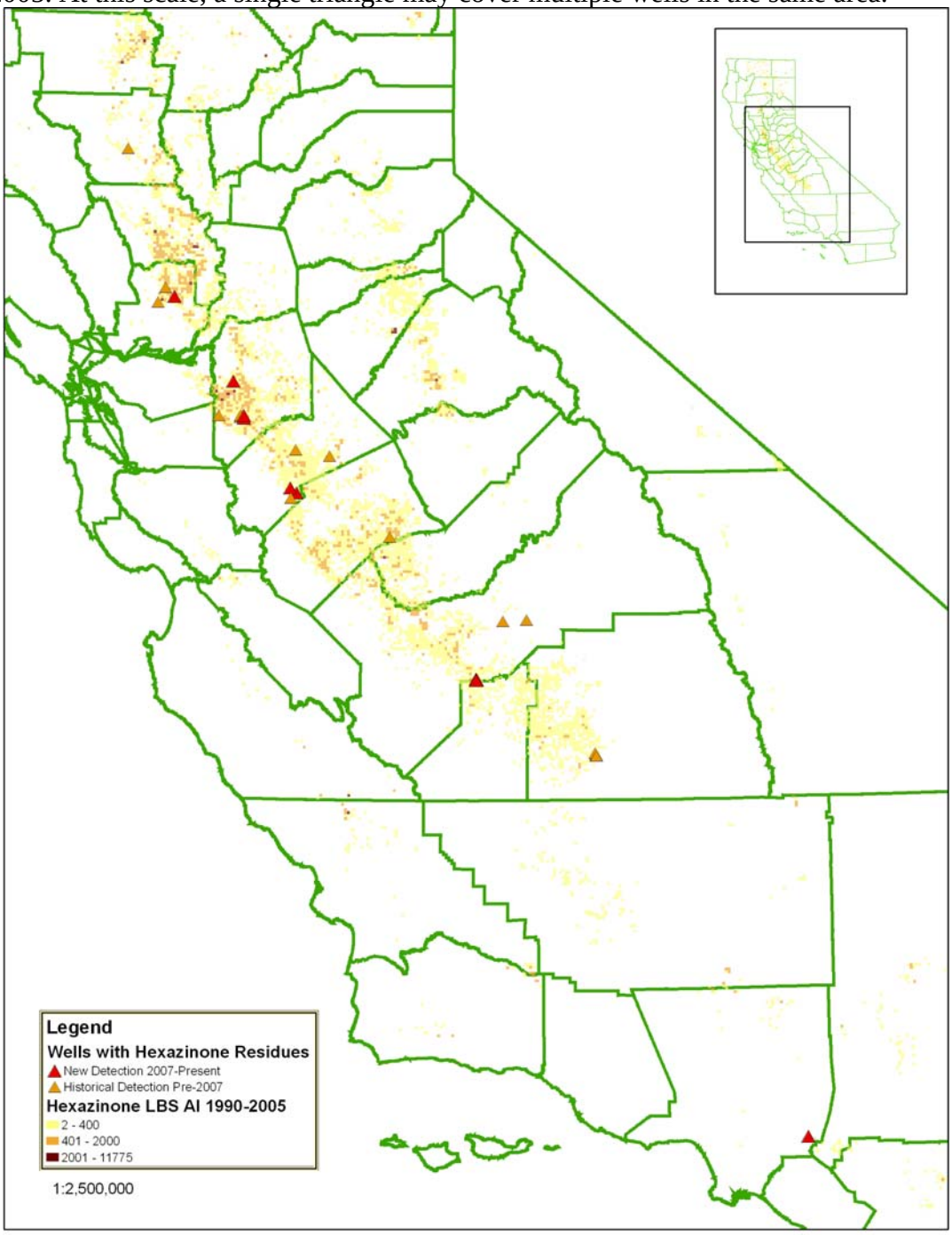


Figure A1-c. Statewide detections of hexazinone in well water and areas where alfalfa has been grown. Alfalfa areas were determined by the summing up the acres where any pesticides have been applied to alfalfa using PUR data, 1990-2005. At this scale, a single triangle may cover multiple wells in the same area.

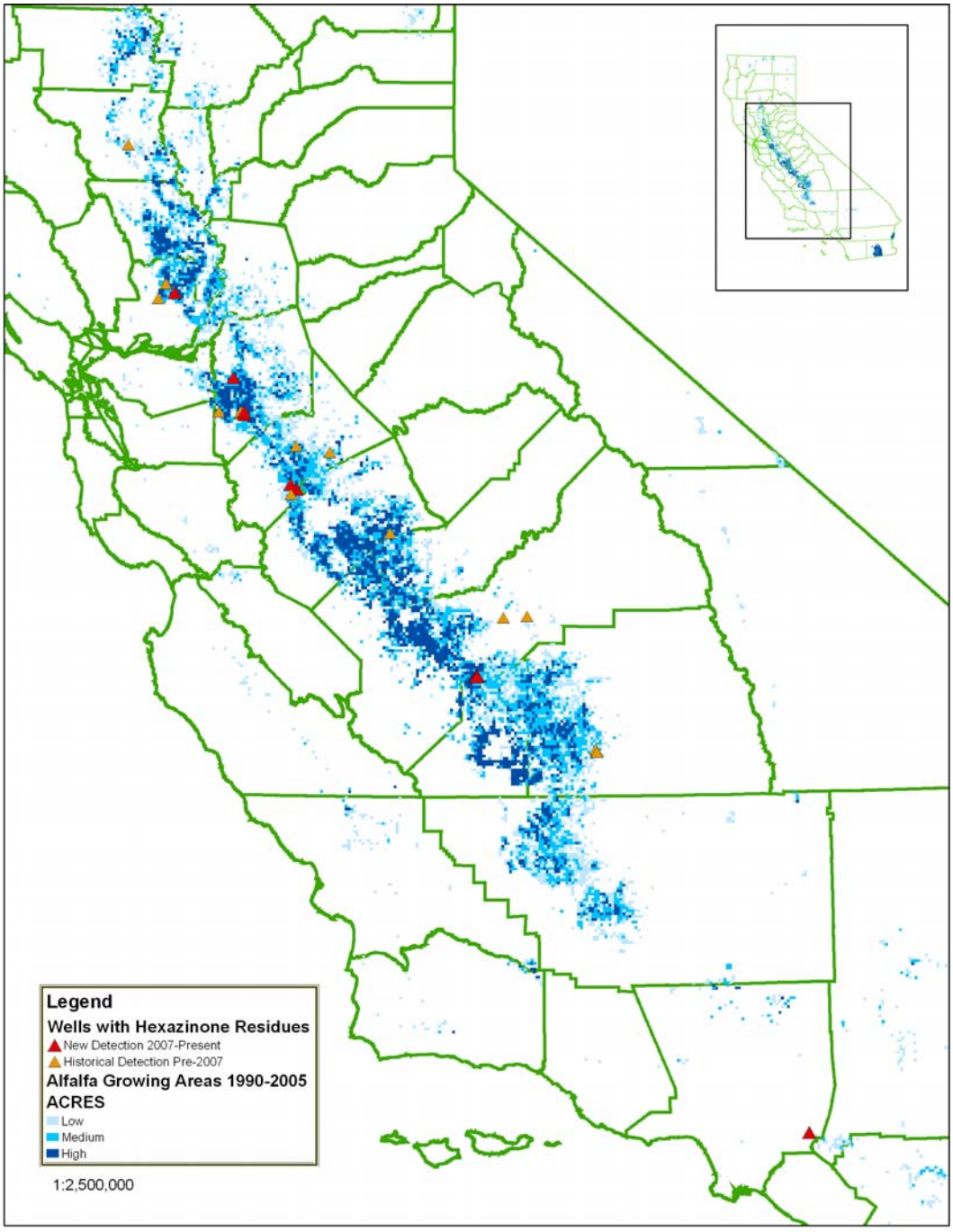


Figure A1-d. Statewide detections of hexazinone in well water and wells that DPR has tested for hexazinone. This data is current through June 2009. At this scale, a single symbol may cover multiple wells in the same area.

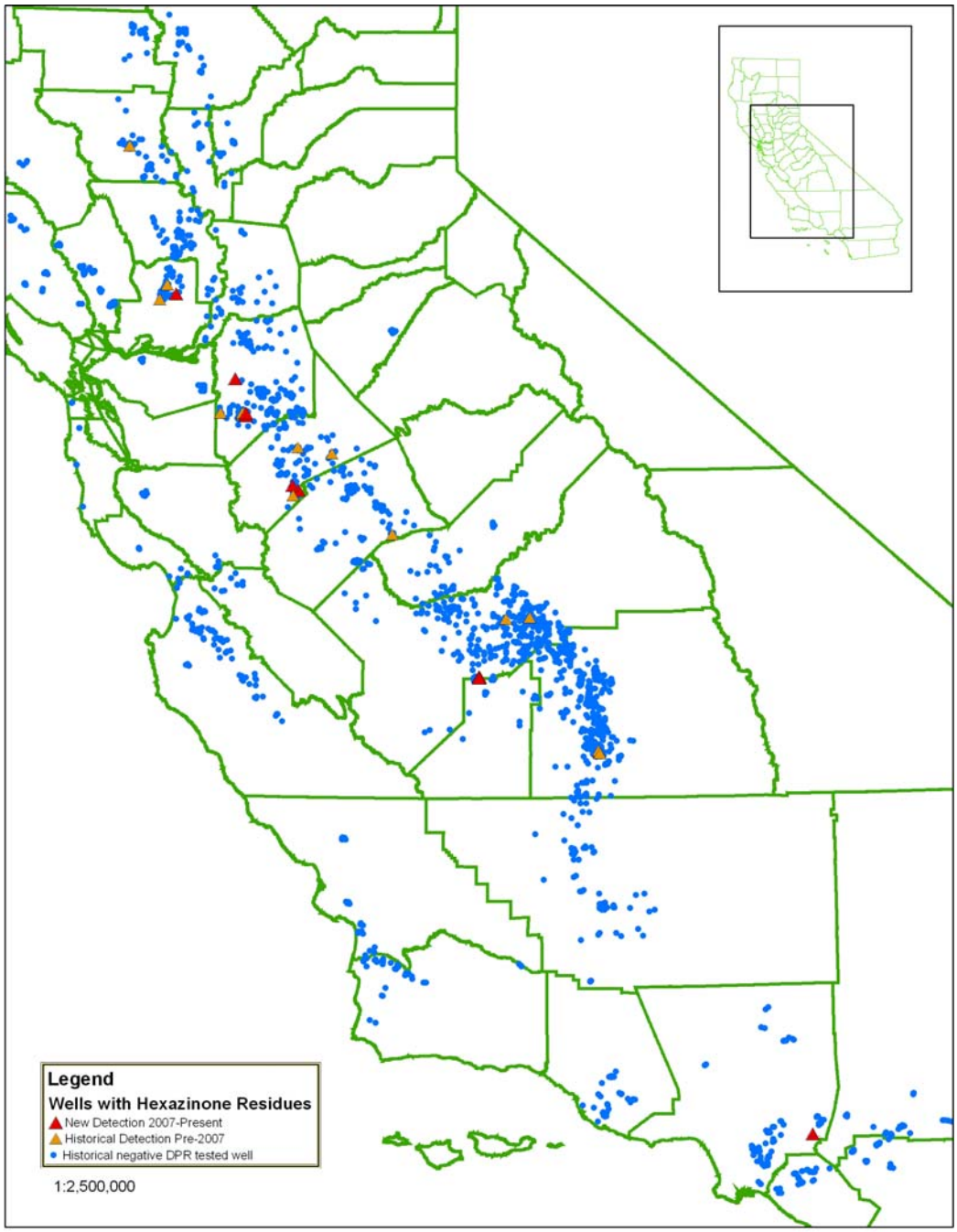


Figure A2. Hexazinone detection in Colusa County and wells sampled by DPR for hexazinone in the vicinity.

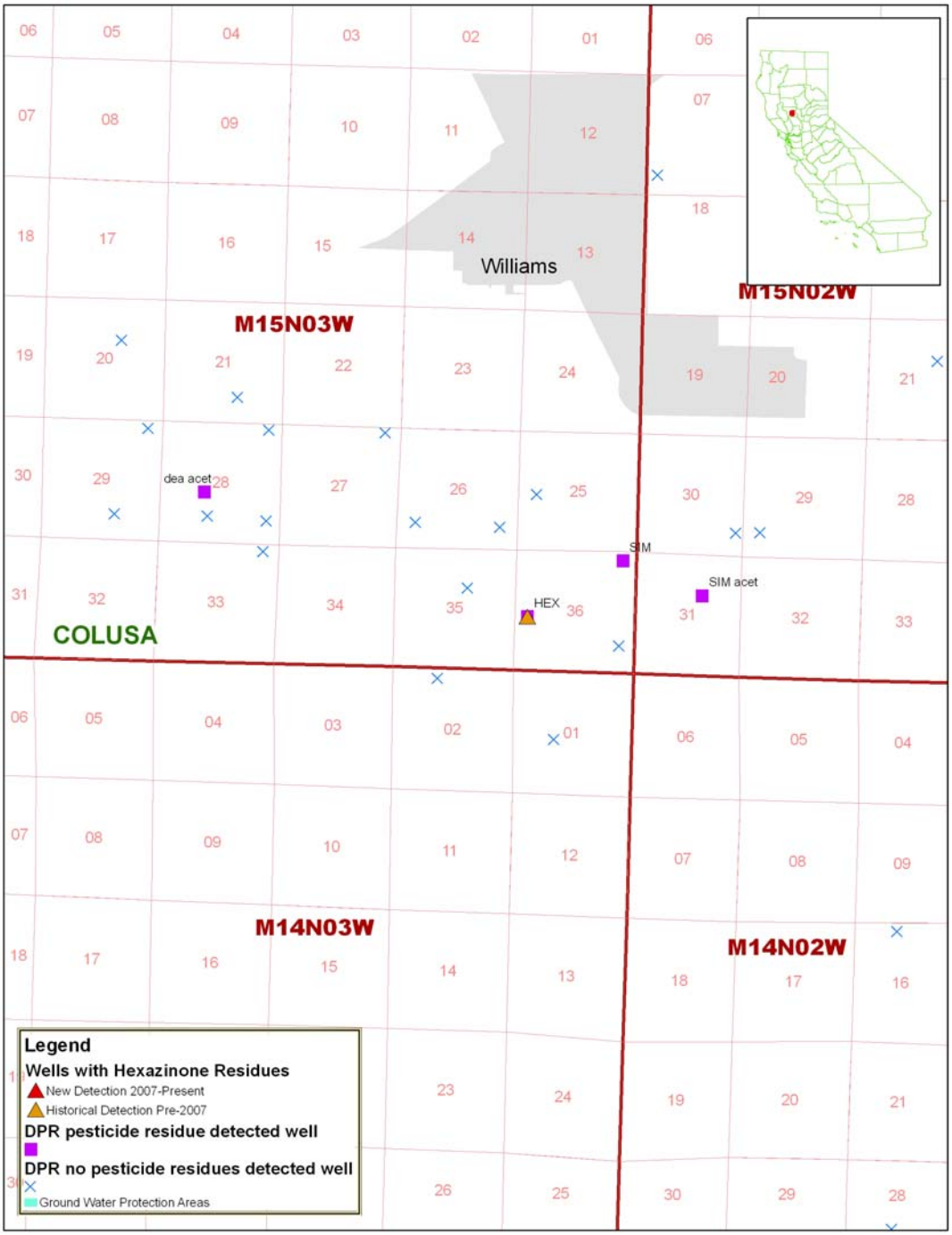


Figure A3. Hexazinone detections in Solano County and wells sampled by DPR for hexazinone in the vicinity.

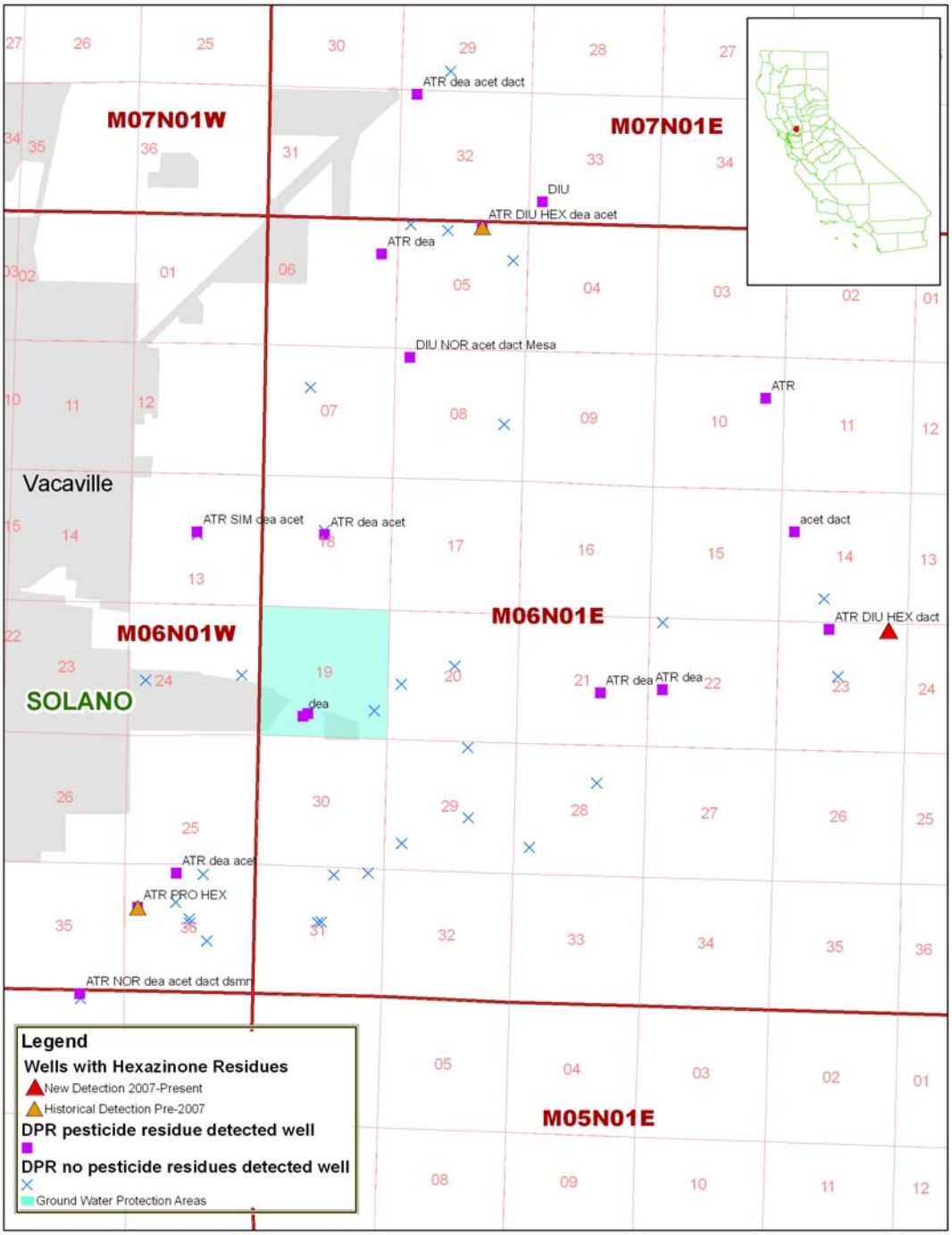


Figure A4. Hexazinone detection in San Joaquin County west of Tracy and wells sampled by DPR for hexazinone in the vicinity.

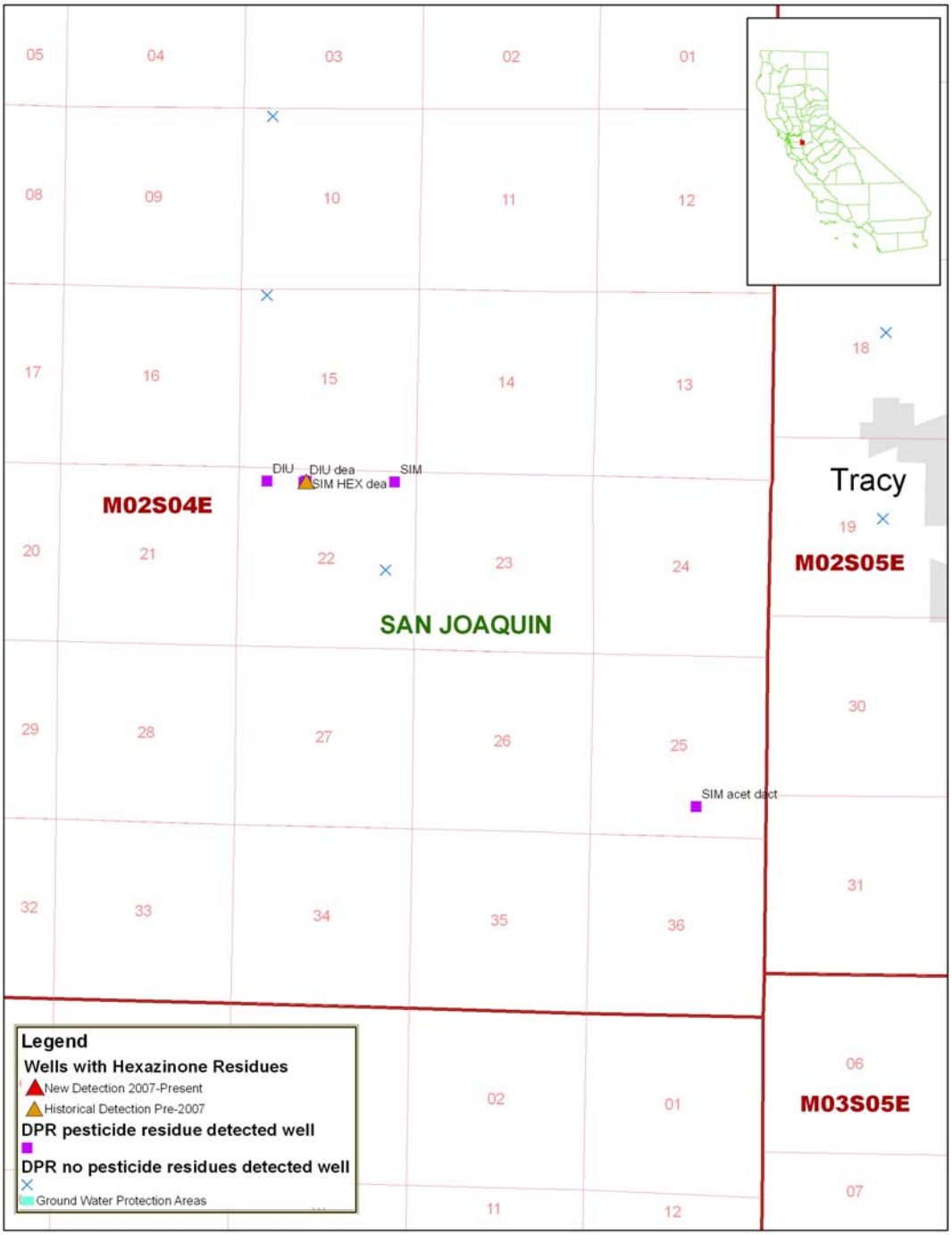


Figure A5. Hexazinone detections in San Joaquin County east of Tracy and wells sampled by DPR for hexazinone in the vicinity. The hexazinone detections were determined to be transitory and not due to legal agricultural use.

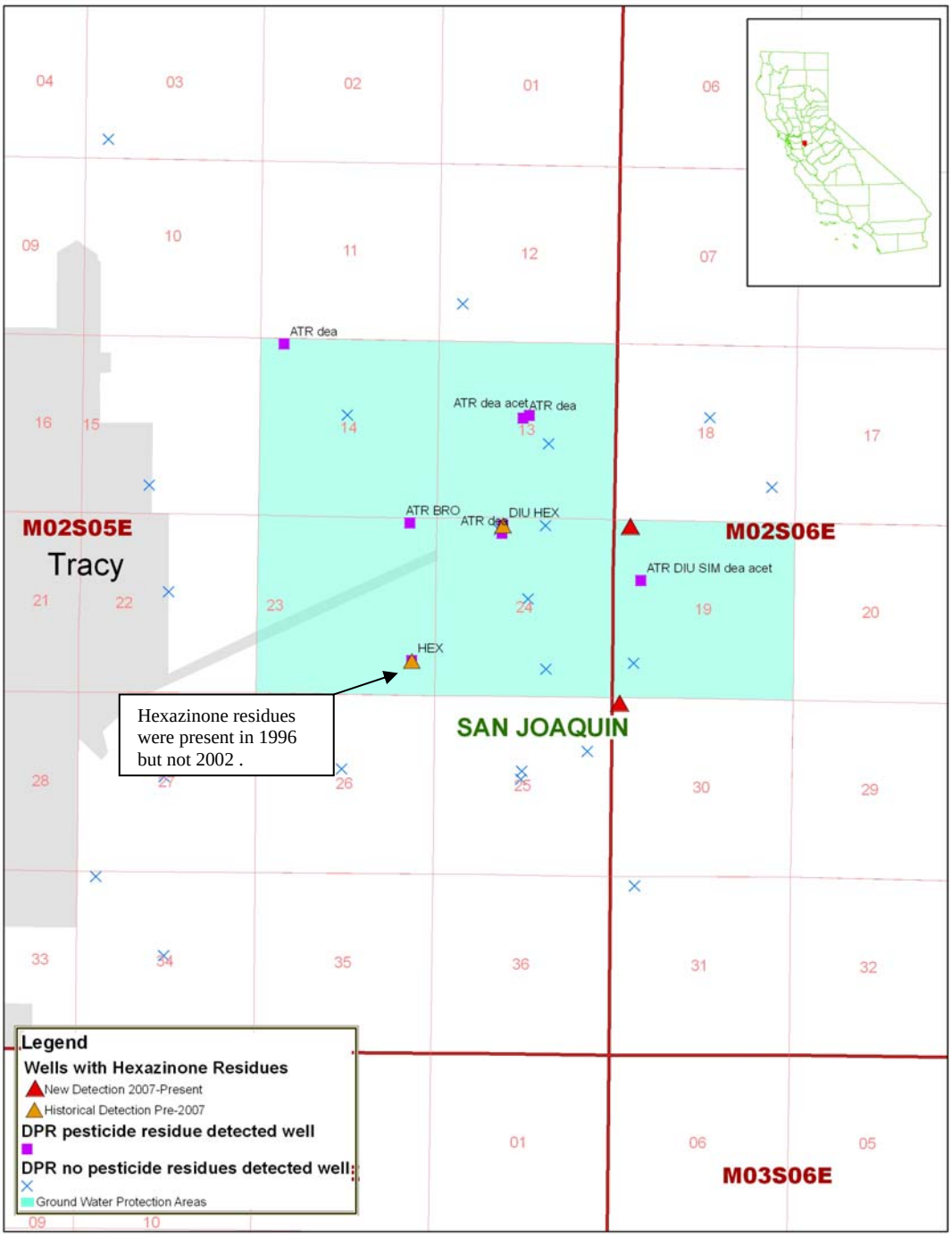


Figure A6. Hexazinone detection in San Joaquin County southwest of Stockton and wells sampled by DPR for hexazinone in the vicinity.

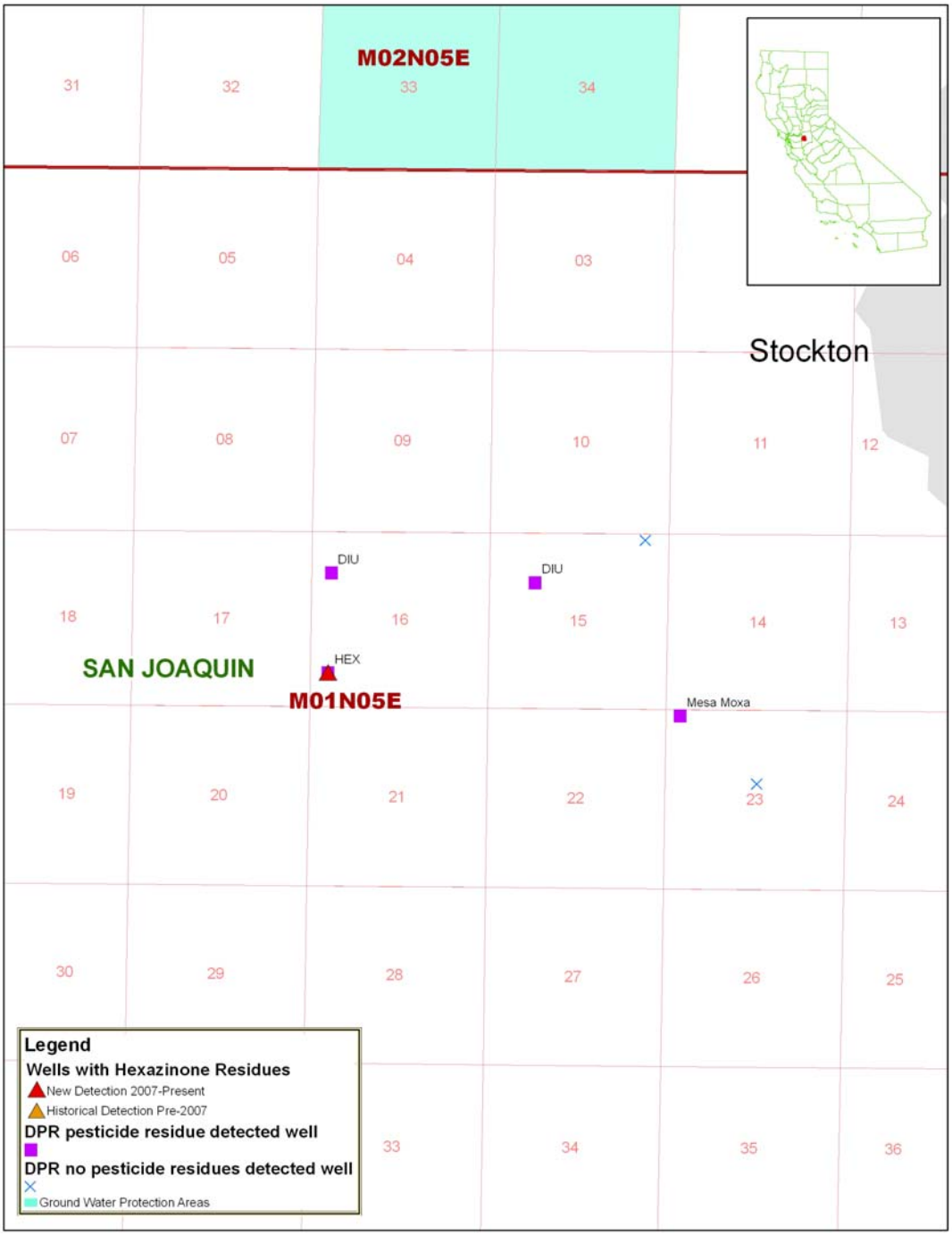


Figure A7. Hexazinone detection in Stanislaus County south of Modesto and wells sampled by DPR for hexazinone in the vicinity.

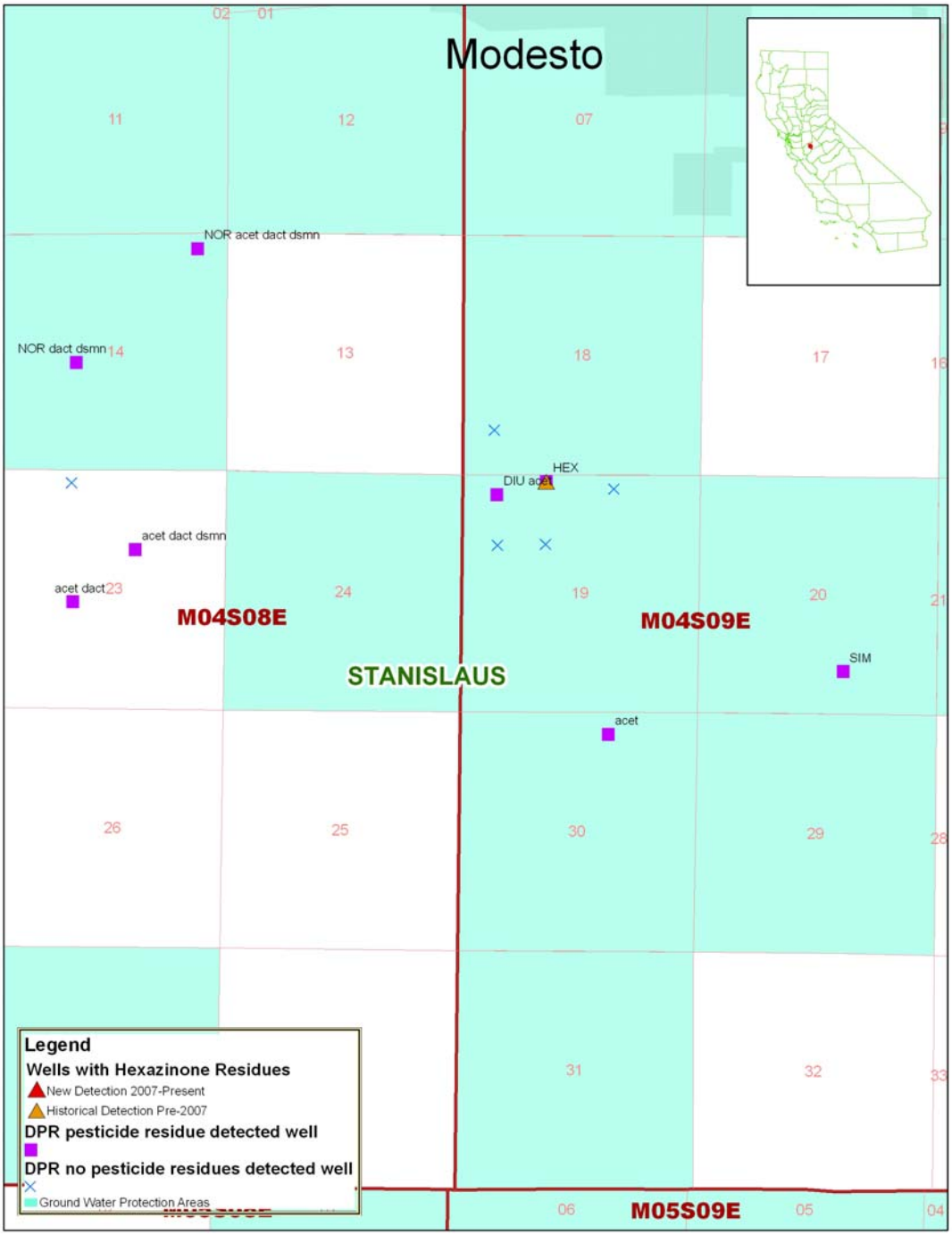


Figure A8. Hexazinone detection in Stanislaus County east of Turlock and wells sampled by DPR for hexazinone in the vicinity.

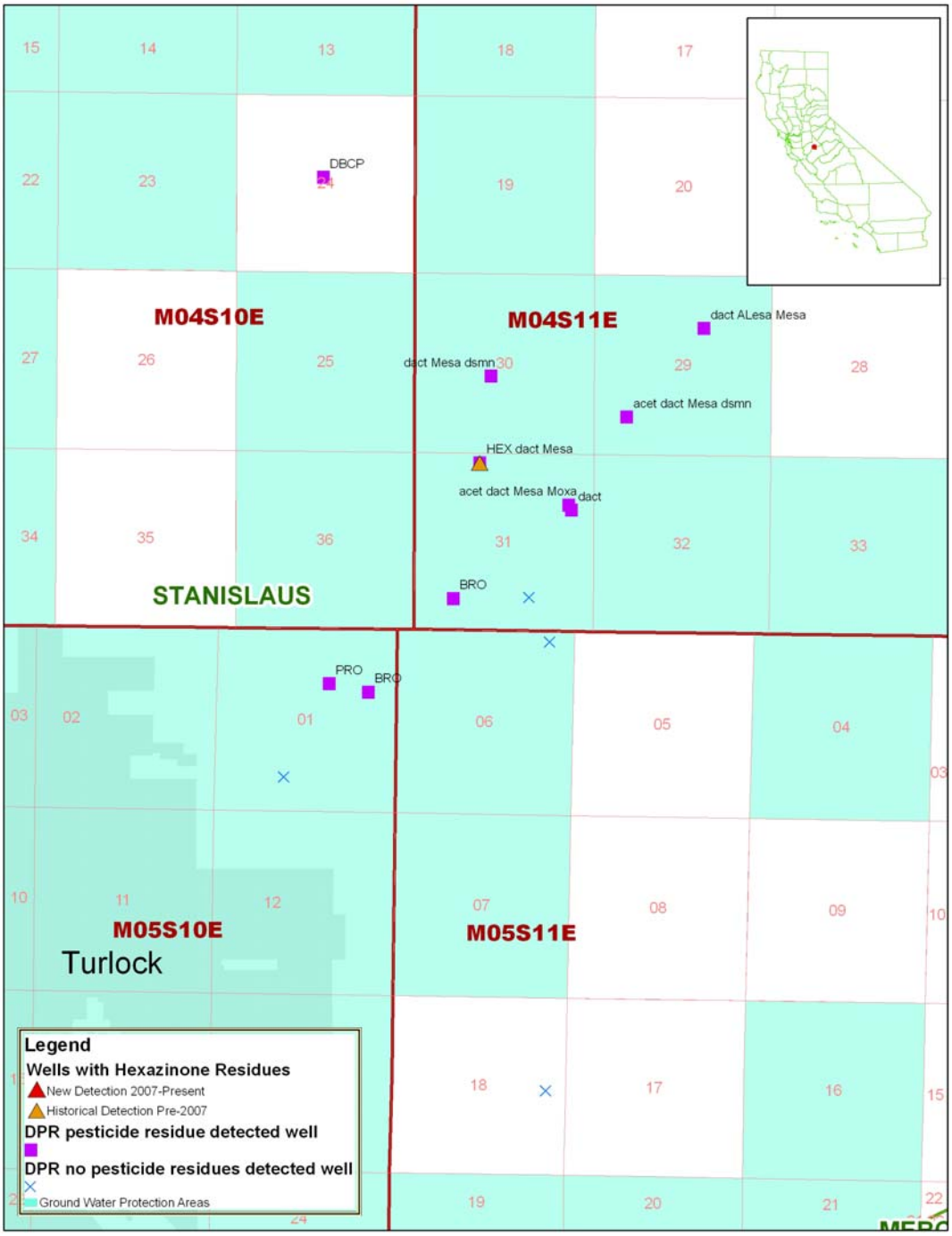


Figure A9. Hexazinone detections in Stanislaus County near Newman and wells sampled by DPR for hexazinone in the vicinity. Further investigation of the Study 240 detections is planned.

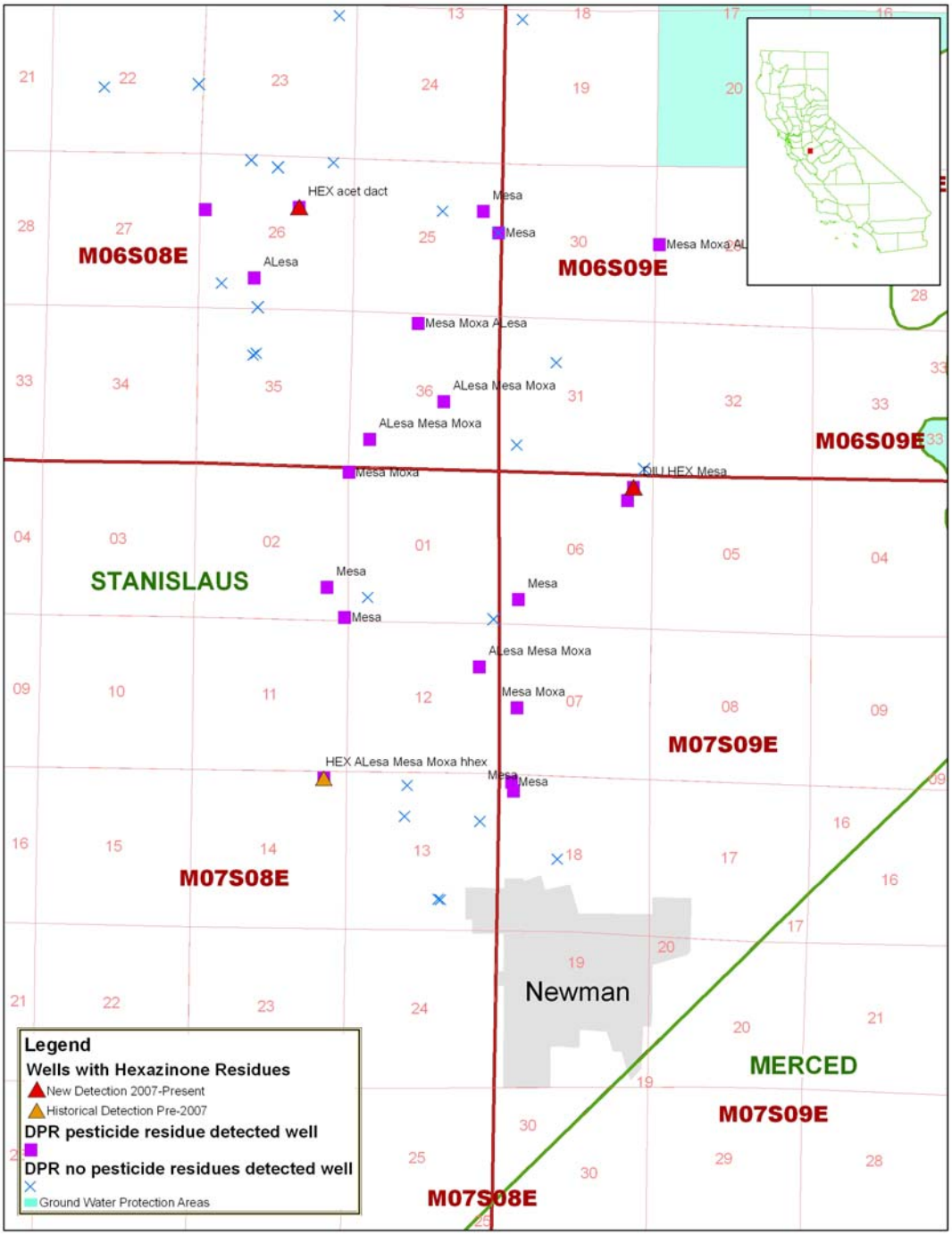


Figure A10. Hexazinone detection in Merced County and wells sampled by DPR for hexazinone in the vicinity.

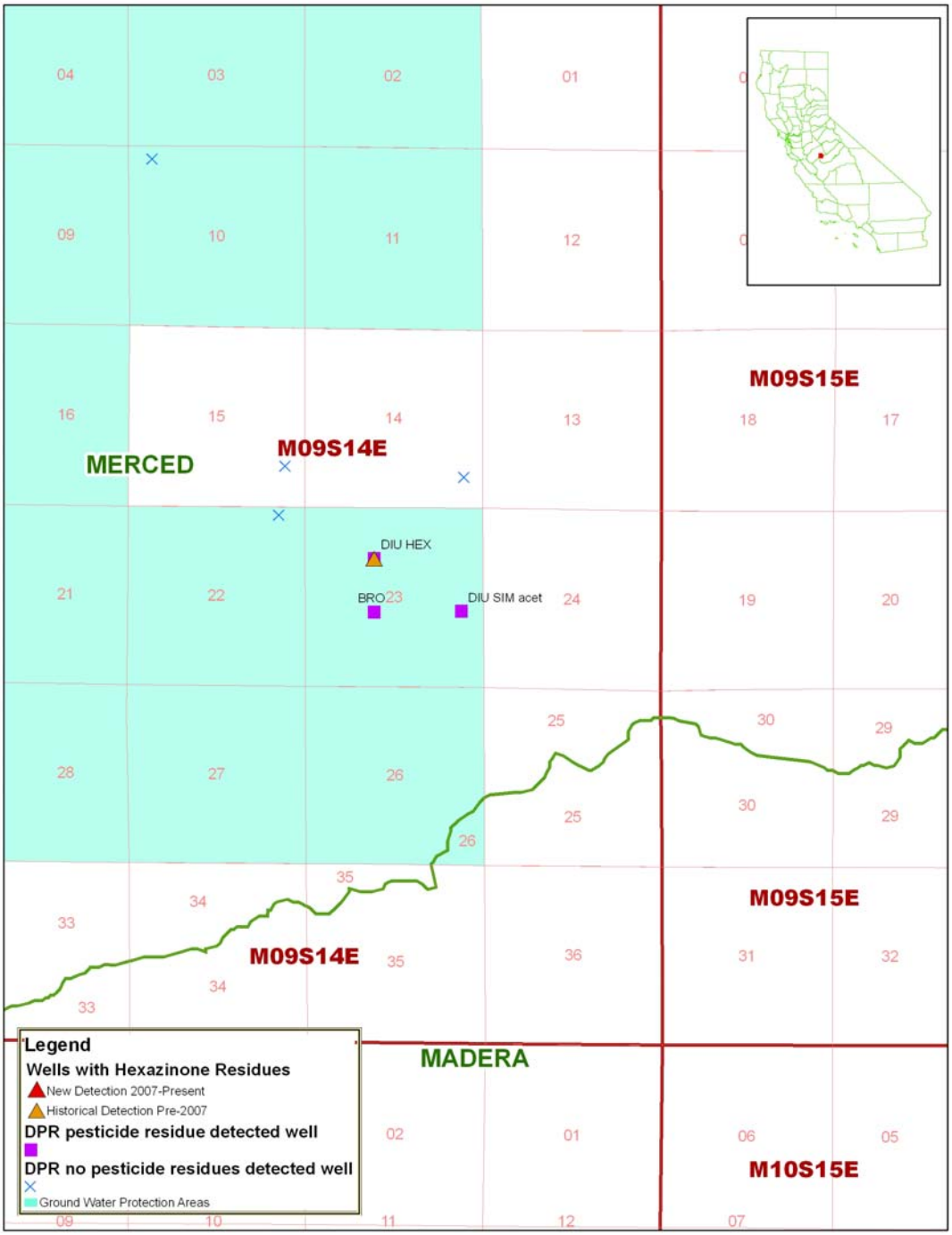


Figure A11. Hexazinone detection in Fresno County near Malaga and wells sampled by DPR for hexazinone in the vicinity.

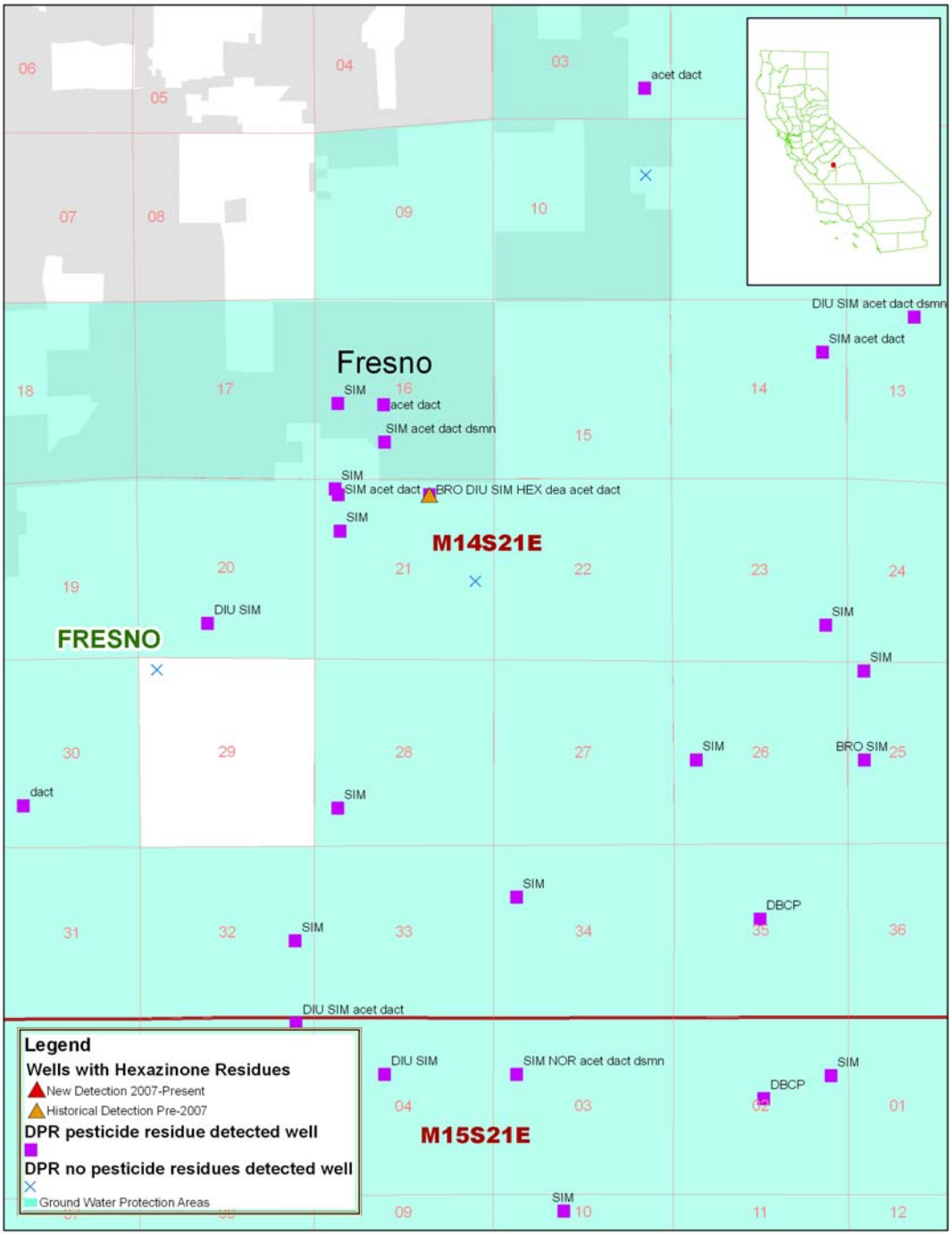


Figure A12. Hexazinone detection in Fresno County near Sanger and wells sampled by DPR for hexazinone in the vicinity.

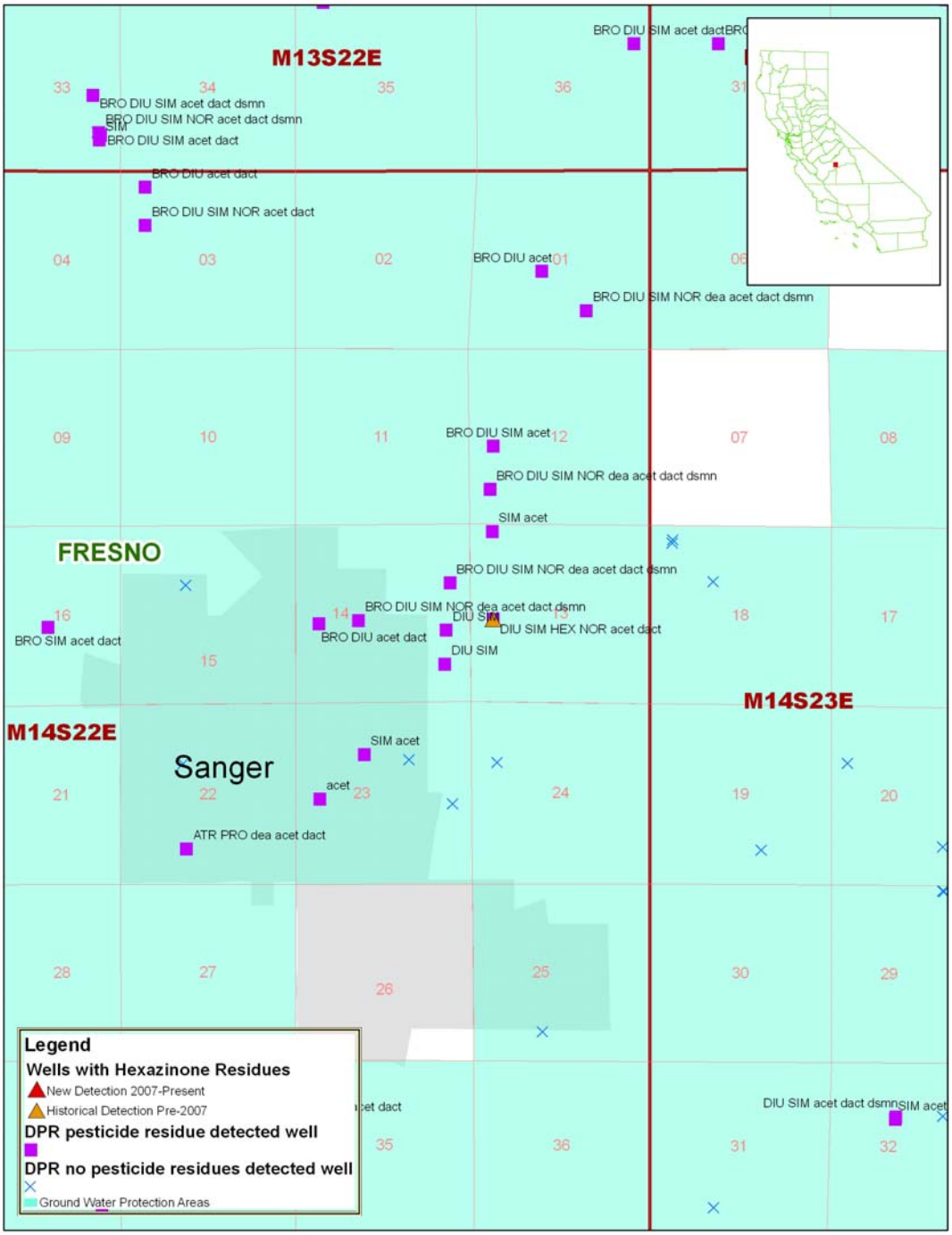


Figure A13. Hexazinone detections in Fresno County near Riverdale and wells sampled by DPR for hexazinone in the vicinity.

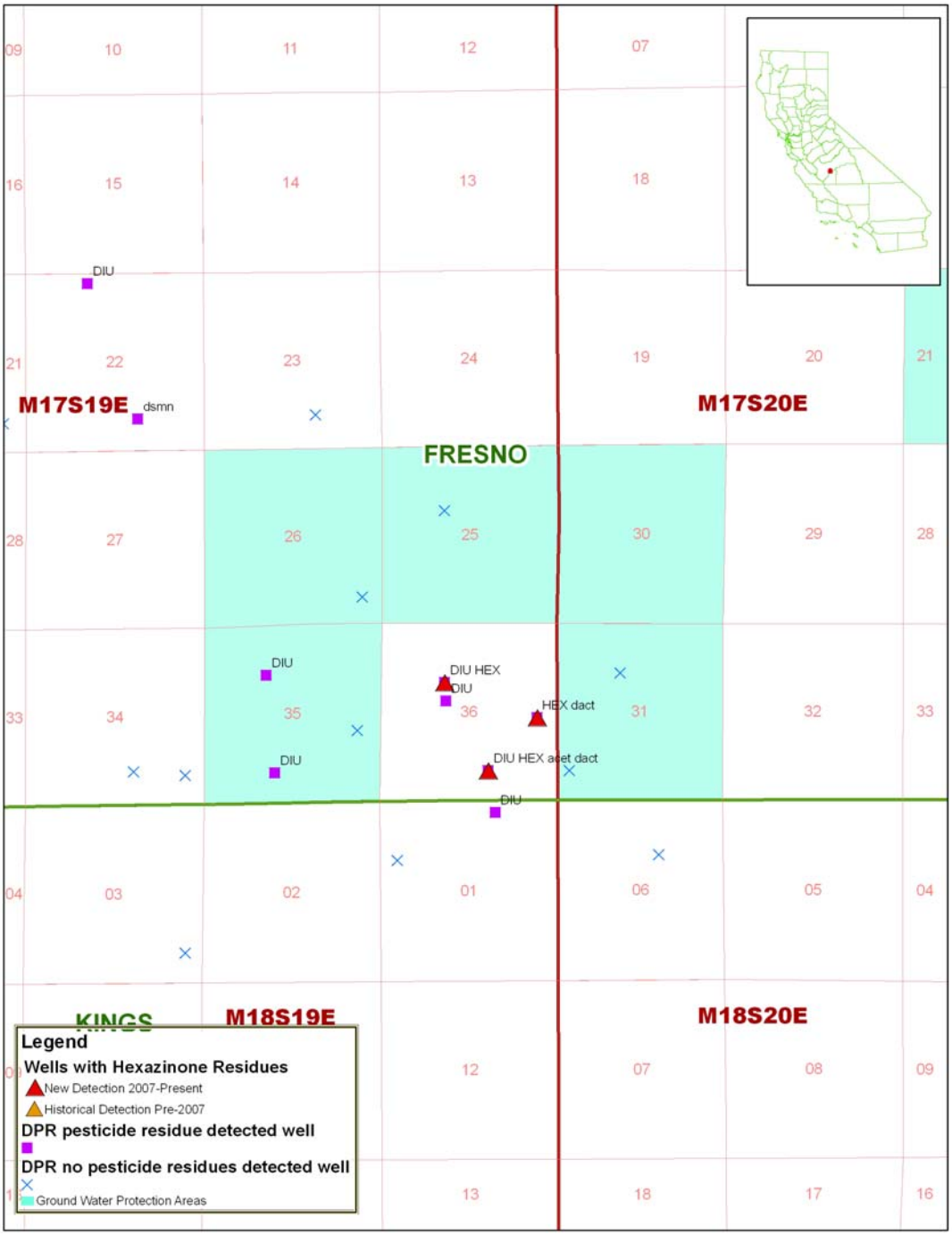


Figure A14. Hexazinone detections in Tulare County near Porterville and wells sampled by DPR for hexazinone in the vicinity. These detections were determined to be due to a point source contamination from the Teapot Dome Landfill.

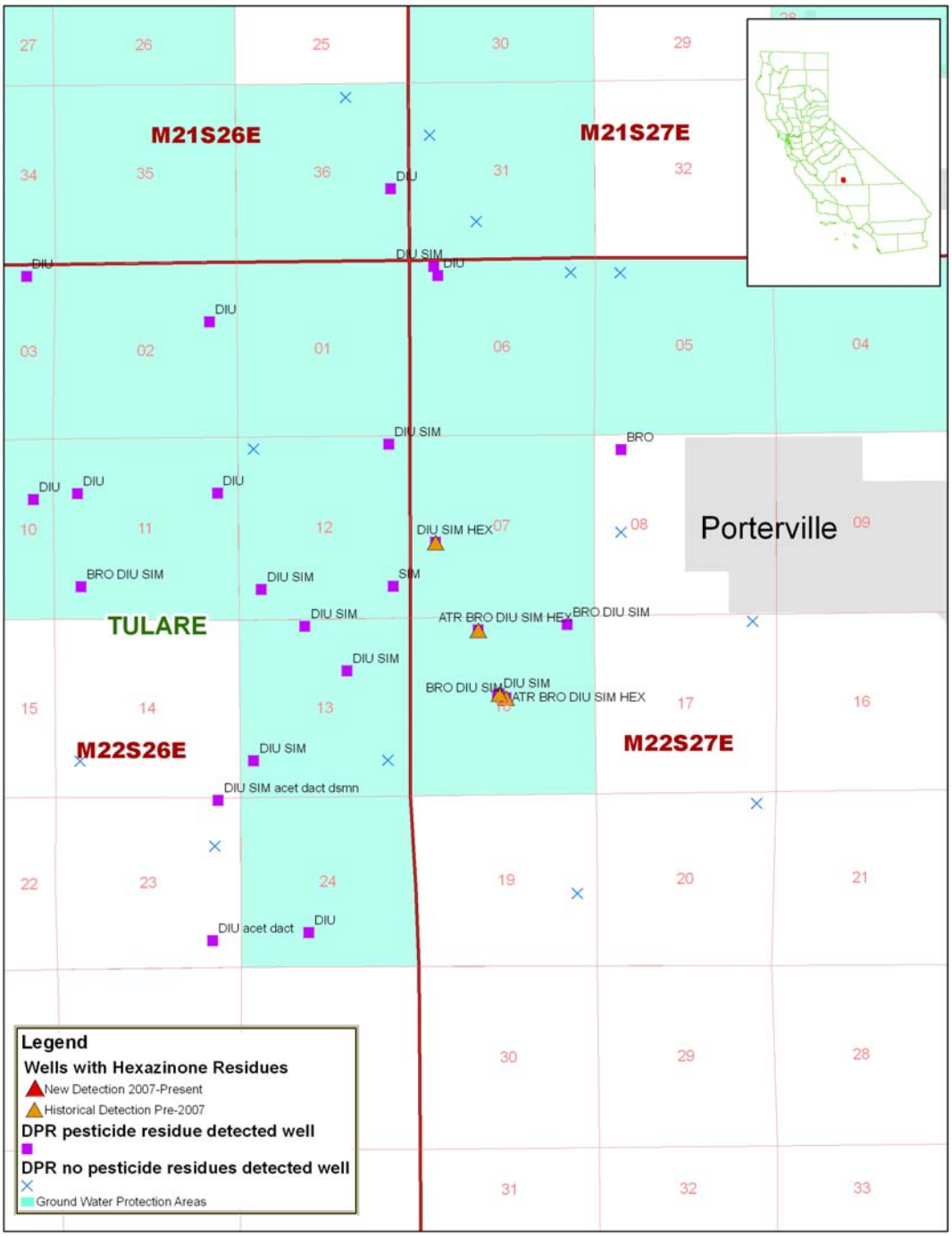


Figure A15. Hexazinone detection in Los Angeles County and wells sampled by DPR for hexazinone in the vicinity. All of these wells were sampled for GW08. Tebuthiuron (TEB) residues were reported in two of the wells. All are currently under investigation.